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Determination of Carbon in Organic Compounds

ANDREW CHALMERS, *Du Pont Rayon Co., Buffalo, N. Y.*

IN SOME fields of research it is occasionally necessary to make rapid determinations of organic compounds by estimating the per cent carbon present. Ordinarily this involves the use of the furnace and combustion tube, a method which requires considerable preparation and time. The method here given was devised for use in estimating the per cent carbon in cellulose compounds, although other organic compounds are readily combustible and results are obtained in from 30 to 45 minutes. Although the range of application of this method is not known, it is mentioned that compounds containing the halogens, nitrogen, or sulfur should be estimated by some other method.

APPARATUS USED

The apparatus used cannot be purchased as a unit. A No. 3 size 500-cc. Erlenmeyer flask, *A*, and a No. 3 size inner cone, *B*, may be purchased from The Scientific Glass Apparatus Company, of Bloomfield, N. J. Pyrex glassware is to be preferred. The inner cone is sealed at the top with a small glass hook, *C*, inserted. The manometer, *D*, consists of Pyrex tubing having an internal diameter of about 3 mm. Millimeter graph paper, cut to required size and pasted onto a piece of stiff cardboard, forms a very efficient manometer scale, *E*. This may be attached to the manometer by paper clips. The thermometer, *F*, is suspended from the hook, *C*, so that it is about 2 cm. from the bottom of the flask. Figure 1 is drawn to scale, making it helpful in constructing the apparatus.

The volume of air enclosed by the mercury is estimated by some approved method such as weighing the apparatus empty, then filling with distilled water, and reweighing, the difference obtained

being equivalent to cubic centimeters of air. Likewise, the volume displaced by the thermometer is calculated and deducted from the initial volume. The volume of air now obtained is a standard and should be marked upon the flask. Vaseline, sulfuric acid, or "sirupy" phosphoric acid may be used for the necessary lubrication of the ground-glass joint.

PROCEDURE

Place 0.07 to 0.1 gram of the sample in the flask and add 2 grams of c. p. chromic acid anhydride. Add, by means of a pipet, 10 cc. of concentrated sulfuric acid in such a manner that the acid does not come into contact with the solids until the stopper has been tightly inserted. Note the temperature of the air inside the flask and also the head of mercury produced by inserting the stopper. Mix the contents, using a gentle centrifugal motion, until the sample has apparently been reacted upon, when heat is cautiously applied to the bottom of the flask. (An enclosed steam bath is suggested.) Continue to heat slowly until the liquid ceases to effervesce, when the thermometer should register about 80° C. Prolonged heating above this temperature leads to evolution of oxygen. Allow to cool until the initial temperature has been reached, when the head of mercury caused by the formation of carbon dioxide is read.

THEORETICAL AND EXPERIMENTAL CALCULATION

V_1 = volume of air enclosed by mercury (minus volume of reagents used) at
 P_1 = atmospheric pressure
 P_2 = pressure exerted by CO₂ plus 760 mm.
 $V_2 = V_1 \times P_2/P_1$
 $V_2 - V_1 = V_3$, volume of CO₂ exerting pressure

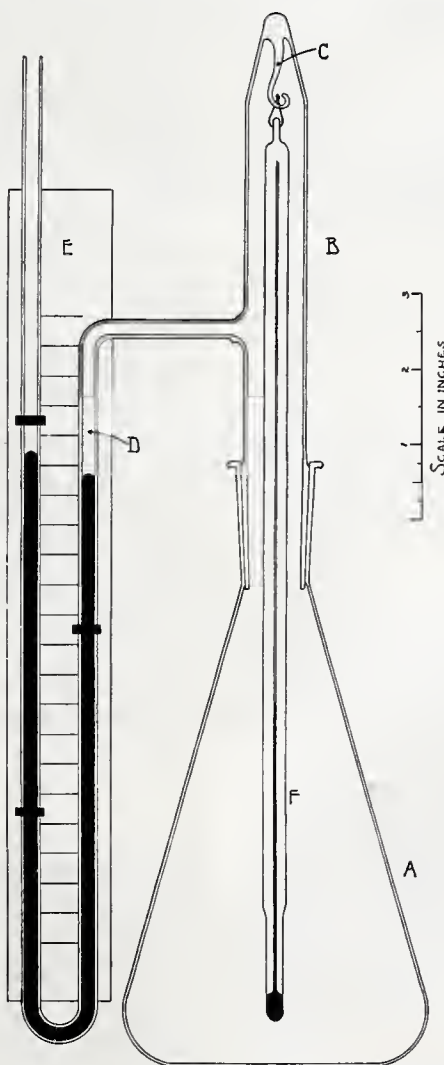


FIGURE 1. SET-UP OF APPARATUS

$$V_3 \times \frac{273}{273 + t} = V_3 \text{ reduced to N. T. P. } (t = \text{temperature of } V_3 \text{ when } P_3 \text{ was noted})$$

As 5.1 cc. of carbon dioxide weigh 0.01 gram at normal temperature and pressure, we obtain

$$\frac{V_3 \times 0.01 \times 3 \times 100}{5.1 \times 11 \times \text{wt. of sample}} = \% \text{ carbon in sample}$$

Cross and Bevan (1), after many experiments, applied the following correction factor which considers the amount of carbon dioxide dissolved in the acid:

$$\frac{\% \text{ carbon obtained}}{25} \times 0.4$$

and this result is added to the per cent carbon obtained above to give the true result.

(a) Using c. p. succinic acid: 0.1025-gram sample; 5 mm. on inserting stopper; 126 mm. final pressure increase; $t = 25^\circ \text{ C.}$; $V_1 = 530.6 \text{ cc.}$

$$\left[\left(530.6 \times \frac{881}{760} \right) - 530.6 \right] \times \frac{273 \times 300 \times 0.01}{298 \times 5.1 \times 11 \times 0.1025} = 40.4\% \text{ carbon}$$

$$\text{and } \frac{40.4}{25} \times 0.4 = 0.64$$

$$40.4 + 0.64 = 41.04\% \text{ carbon (calcd. = 40.6\%)}$$

(b) Using benzoic acid: 68.3 and 68.5% carbon found (calcd. = 68.8%)

(c) Using cellulose: 44.4 and 44.3% carbon found (calcd. = 44.4%)

As mentioned above, the method was originally planned for the analysis of cellulose compounds, and the writer mentions the fact that slightly erroneous results are obtained until one becomes familiar with the operation. Consistent results have been obtained having a maximum deviation of 0.5 per cent from the theoretical carbon content.

ACKNOWLEDGMENT

The writer wishes to acknowledge his indebtedness to Ferdinand Schulze for assistance in constructing the apparatus.

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RECEIVED February 5, 1931.

Calorimetric Determination of Traces of Manganese and Chlorine with Benzidine

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IT HAS been found that when benzidine hydrochloride is added to a very dilute solution containing the permanganate ion or free chlorine, or both, a brilliant blue-green color is produced. The following procedure has application wherever manganese is to be determined as permanganate ion in the absence of free chlorine. Conversely, this reagent may be applied as a test for free chlorine in the absence of the permanganate ion. As compared to the determination of these constituents with ortho-tolidine, or by the direct estimation of the permanganate ion by its color, the following advantages and disadvantages have been noted.

The blue-green color produced by benzidine hydrochloride is much more brilliant and consequently more favorable for colorimetric estimation than the natural color of the permanganate ion or its combination with ortho-tolidine in very dilute solutions.

In the case of the permanganate ion, the most favorable range in which to judge the color produced is that in which the amount varies from 0.0001 to 0.001 mg. in 100 cc. of the solution. The most favorable range in which to judge the color produced by free chlorine is that in which the amount varies from 0.001 to 0.01 mg. in 100 cc. of the solution.

The great disadvantage of this method is the fading of the color produced. In about 2 minutes the blue-green color changes to a yellow-green, which also is not persistent, and therefore the estimation has to be made immediately. This makes the preparation of an artificial color standard necessary. Such a standard can be prepared by mixing solutions of copper sulfate and picric acid.

The presence of large amounts of sulfate should be avoided, since the sulfate ion reacts with benzidine base to produce a white crystalline precipitate which interferes with the accurate judging of the color.

The method employed in this laboratory is as follows:

REAGENTS. Benzidine hydrochloride solution: 2.3 grams of benzidine base dissolved in 100 cc. of 5 per cent hydrochloric acid.

PROCEDURE. A suitable aliquot of the material is taken so that the permanganate ion will be present in an amount between 0.0001 and 0.001 mg., or free chlorine present in an amount between 0.001 and 0.01 mg. The sample is diluted to 100 cc. and 1 drop of benzidine reagent is then added. The sample is immediately transferred to the colorimeter tube and matched against the standard.

The artificial standard is prepared by making a 15 per cent solution of copper sulfate and adding to it the proper amount of 0.5 per cent solution of picric acid to produce the correct tint. After obtaining the identical blue-green tint, which is produced by the addition of the benzidine, the standard is diluted to such a concentration that 100 cc. will match in depth the amount of color produced by 0.001 mg. of permanganate in a solution of known permanganate content. Each cubic centimeter of standard used in matching the color produced will then equal 0.0001 mg. of permanganate ion. Apparently this standard will keep indefinitely without change of color.

A color standard for the determination of chlorine may be prepared in a similar manner.

RECEIVED July 13, 1931.

SUNSHINE VITAMIN MADE IN LABORATORY. A vitamin has been manufactured in the laboratory by strictly chemical methods for the first time in history, Charles E. Bills and Francis G. McDonald of the Mead, Johnson and Co. Research Laboratories, Evansville, Ind., reported at the meeting of the American Association for the Advancement of Science in New Orleans.

They synthesized vitamin D by treating ergosterol with nitrogen monoxide gas and obtained the potent vitamin without ultraviolet radiation. The synthesis of the vitamin is carried out in solution with methyl alcohol, ether, and ethyl acetate at low temperature and with rigid exclusion of oxygen.

SYMPOSIUM ON NEW RESEARCH TOOLS

(Continued)

Presented before the Division of Industrial and Engineering Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931.

Microanalysis of Gases in Relation to Organic and Physiological Chemistry

DEAN BURK AND R. T. MILNER, *Fixed Nitrogen Research Laboratory, Bureau of Chemistry and Soils, Washington, D. C.*

BECAUSE of their property of indefinite expansion and their simple molecular-volume relations, gases offer unique possibilities for quantitative microanalytical determinations. The fundamental elements of the necessary technic have been fairly thoroughly investigated by physicists and physical chemists. More recently organic and physiological chemists have commenced to adapt the technic to their purposes and are at present pointing out future directions of development.

The chief need at present is for the popularization of microanalytical technic among chemists generally by reducing it to ready-made and reasonably simple equipment capable of mass production of routine analyses. Herein lies an opportunity for the skilled and ingenious mechanic to assist the chemist, who is possibly somewhat overawed by the apparent strangeness and delicacy of the apparatus and who shrinks from undertaking the development himself.

GENERAL METHODS OF MICROANALYSIS OF GASES

The various kinds of apparatus devised to analyze small quantities of gas may be divided into two main types. Reference will be made here only to well-known or recently worked-out equipment.

The first type, developed by physicists, measures gases under greatly reduced pressures, employing a McLeod or Pirani gage to measure pressure changes at constant volume, and using solid absorbents or refrigerants to remove the separate constituents of the mixture. It should be capable of dealing with samples of 10 cmm. or less with considerable accuracy. Prescott (16) has developed a rather simple ap-

THIS PAPER presents a brief review of the present general methods and chief problems of microanalysis of gases with particular reference to organic microanalysis, and describes some specific illustrative applications to organic and physiological chemistry of an apparatus which now exists in a highly perfected form and is being used at the Fixed Nitrogen Research Laboratory to study biochemical nitrogen fixation.

paratus in which a combination of Toepler pump and McLeod gage is used to circulate the gas and to measure the pressure. The gas is circulated through small amounts of solid absorbents, such as P_2O_5 , soda lime, and hot copper oxide. The apparatus is all glass with mercury cutoffs and without stopcocks. An accuracy of about 0.1 per cent in a 15-cmm. sample is obtainable. Langmuir (12) and Ryder (17) with a similar apparatus have used with success baths of liquid air and solid carbon dioxide for the removal of permanent gases, water vapor, and carbon dioxide. In this connection may be mentioned the work of the laboratories of the General Electric Company and the Bell Telephone Company on degassing metals and on the effect of slight traces of gases on electron emission of filaments; in these cases gas pressures were investigated corresponding to surfaces covered from a fraction of a monomolecular layer to multiple molecular layers.

The second type, developed chiefly by chemists, as might be anticipated, involves working with gases under normal pressures with an apparatus which somewhat resembles the usual Orsat, with, however, all parts much smaller. Blacet and Leighton (1) describe an apparatus with a capillary-tube buret of 0.5 mm. diameter holding 112 cmm. and using mercury as the confining liquid. The apparatus is relatively simple to construct and to handle, and its accuracy of from 0.3 to 1 per cent can no doubt be improved. Attempts to use this type of apparatus for even smaller amounts of gas have led to the measurement of the diameter of a single gas bubble under a microscope after successive respective treatments with different liquid absorbents.

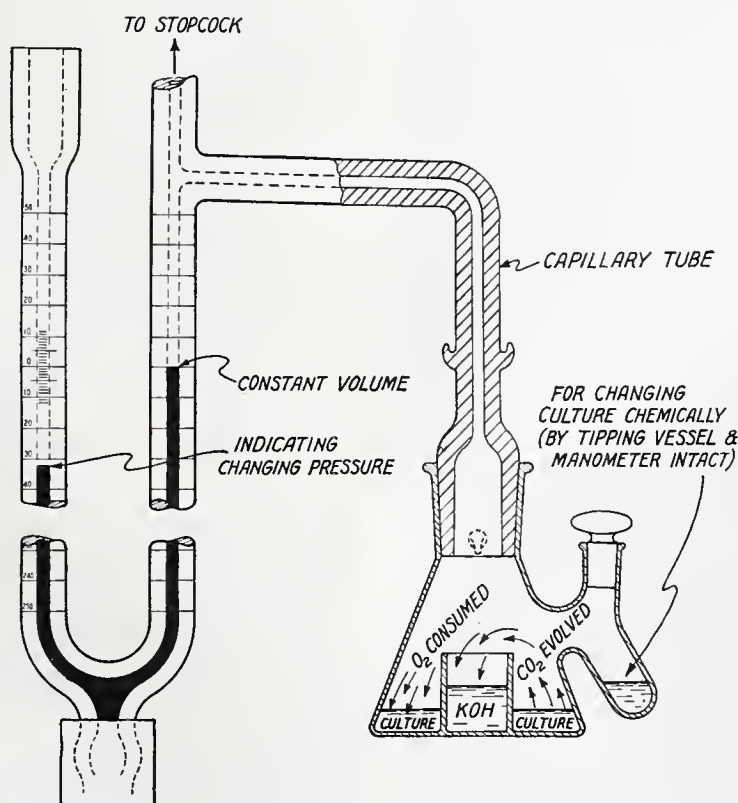


FIGURE 1. DIAGRAM OF WARBURG MANOMETRIC APPARATUS

Three other less generally employed types of apparatus may be mentioned. Campbell (10) used the characteristic vapor pressures of the several gases, measured with a Pirani gage, to analyze small amounts of gas. He did not claim great accuracy, but the method possesses possibilities and is rapid. Refrigerants rather than absorbents were used to

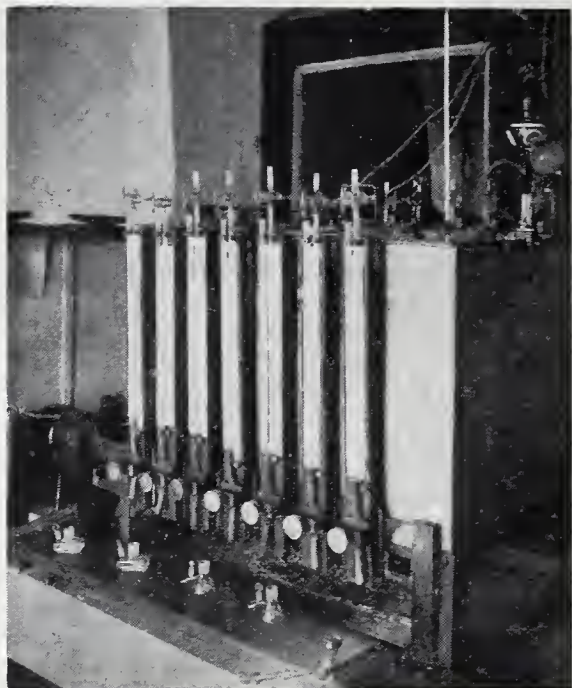


FIGURE 2. MANOMETERS MOUNTED IN BATH

remove the separate constituents from the mixture. Weaver (23) and others at the Bureau of Standards have developed the thermal-conductivity method of gas analysis to a considerable degree, and this may be modified to involve very small amounts of gas. Spoehr and McGee (19) in 1923, and others more recently, have developed an electrical-conductivity method for determining small amounts of carbon dioxide for use especially in photosynthesis studies.

PRESENT PROBLEMS OF ORGANIC MICROANALYSIS

Owing to the work of Pregl (15), a satisfactory analysis for carbon and hydrogen can now be made on from 3 to 5 mg. of material. Lately, attempts by Niederl and Meadows (14) have been made to refine this technic, and samples from 1 to 2 mg. have been handled. The application of microanalysis of gases should give greater accuracy with even smaller samples.

There are two problems to be solved in this latter respect. First, the organic sample must be converted completely to known gases by combustion in oxygen or by some other process. If it is possible to form gases all of which can be determined, no analytical balance will be needed. This should be easily possible with compounds containing only carbon, hydrogen, and oxygen. Organic nitrogen compounds, particularly nitro compounds, offer great difficulty, since a part, at least, of the nitrogen is converted to nitrogen dioxide (oxygen in excess), and the gas analysis becomes unsatisfactory. The presence of halogens, sulfur, or phosphorus would introduce additional difficulties. If the use of a balance is to be avoided, some method of handling these elements must be worked out. However, if a balance is used to weigh out only the sample, the determinations of carbon and hydrogen can be carried out very conveniently by gas analytical methods.

The second problem, that of accurately determining small quantities of carbon dioxide and water vapor, has been largely solved by above-mentioned workers (10, 12, 17). The problem is simplified in that only two gases need to be determined, with no need for further combustions. It may be of

advantage to transform the water vapor into some other form, and the use of calcium hydride (yielding hydrogen) or of a naphthyl chlorhydrin (yielding hydrochloric acid) has been suggested. A typical organic compound of, say, 30 per cent carbon and 2 per cent hydrogen, should be susceptible to an analytical accuracy of 0.1 per cent, using a 0.5-mg. sample.

SPECIFIC APPLICATIONS OF WARBURG APPARATUS

Otto Warburg (21, 22) of Berlin has developed a general technic which yields variations in procedure to suit almost any specific problem involving kinetic gas exchanges or gas analyses, and which may be carried out with a relatively high degree of accuracy, delicacy, and speed of operation. Before the development of this technic, most biochemical and physiological studies involved macrochemical quantities of material, and when cultures of various organisms were employed several days or weeks were required to perform an experiment. It is no exaggeration to state that this new technic reduces the time, labor, and materials involved ten to fifty fold. It has so far received little attention in America, and yet its widespread use deserves the strongest recommendation.

Figure 1 (9) shows one of the more common forms of apparatus used for kinetically measuring oxygen consumption as a function of time, under conditions of constant tempera-

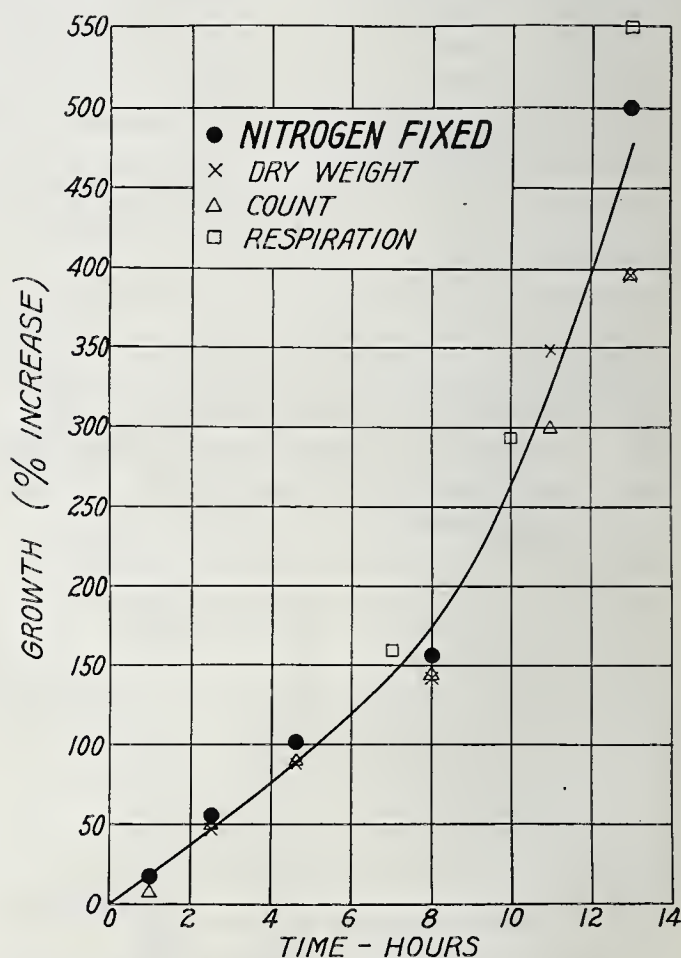


FIGURE 3. PROPORTION OF FIXATION QUANTITIES TO GROWTH INCREASES

ture and atmospheric pressure. The total volume of the vessel measured to the right-hand level of the manometric fluid (Brodie solution) is about 15 cc., 2 cc. of which are occupied by the oxygen-consuming solution under investigation, and 0.30 cc. by the liquid absorbent used to absorb any gases involved, such as carbon dioxide, and the remaining volume by gas. The right-hand level of the manometric fluid is held constant to provide conditions of constant volume; any oxygen consumption causes a very slight decrease in the internal pressure of the system which is registered by a fall in the left-hand level. The reading thus obtained, when

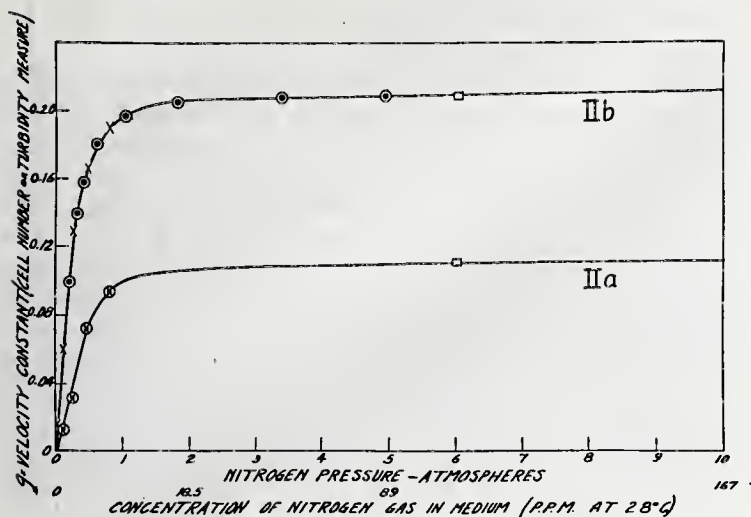


FIGURE 4. GROWTH-VELOCITY CONSTANT VERSUS NITROGEN PRESSURE. With (IIb) and without (IIa) the growth stimulant humic acid

multiplied by a constant characteristic of the vessel, gives directly the number of cubic millimeters of oxygen consumed. The vessel constant depends upon the temperature, volumes of gas and liquid, the Bunsen absorption coefficient of the gas in the liquid, and the normal pressure of the manometric fluid, and generally varies from 0.5 to 2. If it is desired to change the chemical environment of the investigated solution during the course of an experimental run, a 0.10-cc. portion of a solution of the chemical, made up to twenty times the desired concentration, is placed in the side-cup initially and then tipped in when desired.

Figure 2 (9) shows the manometers mounted in the thermostated water bath, the vessels being submerged and hidden from view. Fourteen manometers are accommodated, making a large number of simultaneous experiments possible. The manometers are shaken at the rate of about 120 cycles per minute with an amplitude at the height of the vessels of about 3 cm. The temperature of the bath is maintained constant to 0.01°C . Some of the unattached vessels are illustrated in the foreground.

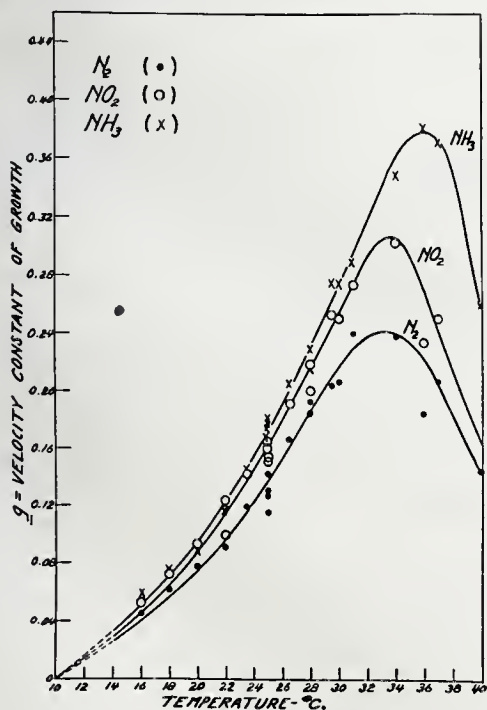


FIGURE 5. VELOCITY CONSTANT AS FUNCTION OF TEMPERATURE

In general, gases measured or analyzed by the Warburg technic are usually determined to limits of about 0.5 mm., but by making microscopic manometric readings and other com-

plementary refinements, the delicacy may be increased some fifty fold, to 0.01 mm. By variation in method it is possible to measure more than one gas simultaneously, where significant solubility differences obtain, as in the case of carbon dioxide and oxygen in water; several vessels and simultaneous equations are employed in this more complicated procedure. Differential manometers are also employed in the Warburg technic, generally being shaken at much higher speeds than the manometers illustrated in Figure 2. Needless to say, there are numerous types of vessels in use other than that shown in Figure 1.

APPLICATION IN VARIOUS STUDIES. In general, the Warburg technic has so far had little application outside the fields of physiology and biochemistry, where it has been used to study the consumption or production of various gases, such as oxygen, carbon dioxide, hydrogen, nitrogen oxides, carbon monoxide, etc., in studies of respiration, fermentation, glycolysis, photosynthesis, protein decomposition, muscle and cancer metabolism, nitrate reduction, blood charcoal oxidation, and the determination of the chemical constitution of the respiration enzyme. Emil Warburg (20) studied the velocity of ozonation. At this laboratory it has also been

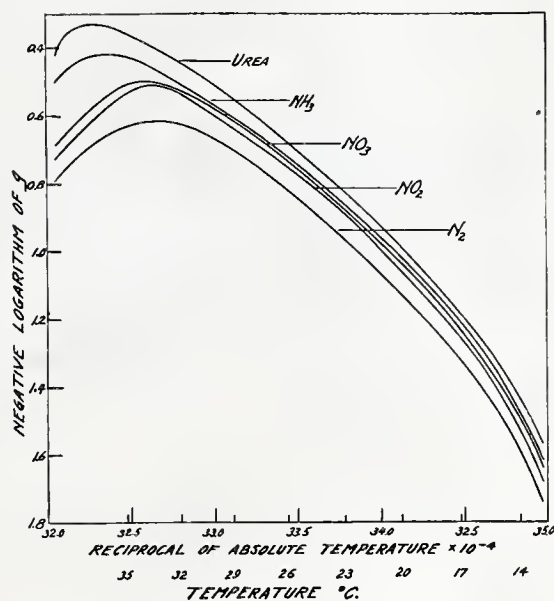


FIGURE 6. REPLOT OF FIGURE 5

used (2) to analyze for oxygen. By placing slightly acidified pyrogalllic acid in the side-cup (see Figure 1) and alkali in the vessel proper, filling the system with the gas to be analyzed, allowing the whole system to come to thermal equilibrium, and then mixing the pyrogalllic acid with the alkali, it is possible to measure in a few minutes percentages of oxygen ranging from 0.01 to 3 per cent. Greater percentages may be measured if certain adjustments are made to refill the system with an inert gas as the oxygen is absorbed by the pyrogallol beyond the extent of 3 per cent, which is the scale-reading capacity of the manometer. Other gases can be analyzed similarly where the absorbent may consist of two components which are inactive until mixed, after thermal equilibrium has been attained.

Brought to the attention of organic chemists in particular, the Warburg technic should prove a valuable tool not only for analyzing gases as just indicated, but also for measuring the kinetics of reactions. It is not necessary, for instance, that some gas be directly involved in the reaction under study. If some change in hydrogen-ion concentration could occur, for instance, and the solution contain bicarbonate buffer, it would be possible to have this change indicated by a change in the carbon dioxide tension in the gas phase. This method has been followed by Krebs (11) in studying fermentative protein-cleavage.

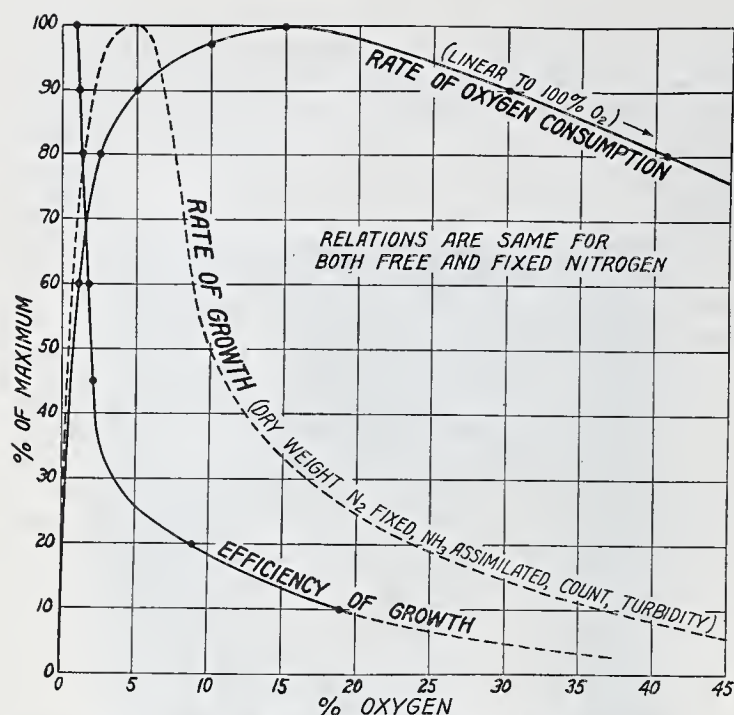


FIGURE 7. RATE OF OXYGEN CONSUMPTION AND RATE AND EFFICIENCY OF GROWTH AS FUNCTIONS OF OXYGEN PRESSURE

APPLICATION TO BIOCHEMICAL NITROGEN FIXATION. At the Fixed Nitrogen Research Laboratory the Warburg technic has been adapted to studying nitrogen fixation by micro-organisms, such as *Azotobacter*, the fixation process occurring at ordinary temperatures and pressures. Our purpose in presenting the results to follow is to illustrate rather than to emphasize findings with respect to nitrogen fixation.

Fixation is indicated by an increase in the rate of oxygen consumption, which is caused by the growth of the organisms, and this in turn is dependent upon nitrogen fixation. All three quantities are proportional to one another, as found by experiment. These quantities are also proportional under

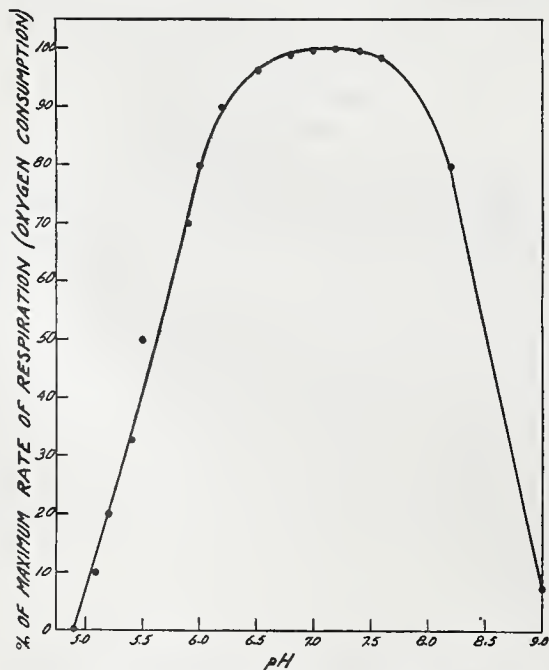


FIGURE 8. RESPIRATION OF *Azotobacter* AS FUNCTION OF pH

ordinary conditions to growth increases as measured by dry weight, cell number, or turbidity, as indicated in Figure 3 (8). The ratio of nitrogen fixed to oxygen consumed is only about 1 to 100 so that the amounts of nitrogen measured in the apparatus shown in Figure 1 correspond to only 0.01 to 1 cmm., or about 10^{-5} to 10^{-3} mg. of nitrogen. With technic

involving microscopic reading of the manometers, 10^{-7} to 10^{-5} mg. could be determined.

Figure 4 (8) shows the function obtained when the monomolecular growth-velocity constant, g , is plotted against nitrogen pressure; it is seen to represent a rectangular hyperbola similar to that employed by Langmuir to express the amount of gas adsorbed in a monomolecular layer at catalytic surfaces with varying gas pressures. Figure 5 (13) shows the velocity constant as a function of nitrogen pressure over a wide range of temperature, and Figure 6 (13) is a replot of the data, yielding curves whose slopes at any point represent empirically the Arrhenius heat-of-activation constant of growth. In all of these cases the g value in experiments conducted with nitrogen represents the velocity constant of both growth and nitrogen fixation. Figure 7 (3) shows rate of oxygen consumption, rate of growth, and efficiency of growth

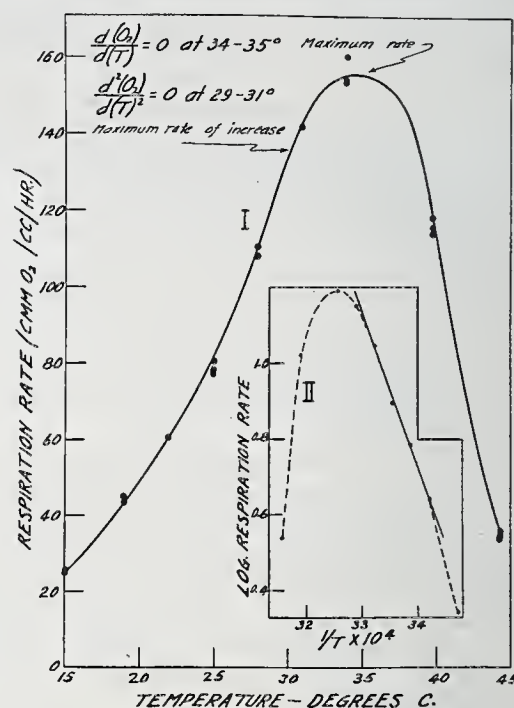


FIGURE 9. RESPIRATION OF *Azotobacter* AS FUNCTION OF TEMPERATURE

as functions of oxygen pressure. Figure 8 (5) shows respiration of *Azotobacter* as a function of pH, and Figure 9 (13), respiration as a function of temperature. In presenting these various figures it is not desired to stress the detailed points of physiological interest, but merely to indicate the nature of the independent and dependent variables studied, as indicated by the ordinate and abscissa designations.

As definite accomplishments in applying the Warburg technic to biochemical nitrogen fixation, the following may be cited, in addition: Nitrogen fixation has been demonstrated by absorption of nitrogen gas, rather than by chemical micro-Kjeldahl analysis (2); the great majority of biochemical functions of *Azotobacter* obtain identically in free and fixed nitrogen, and hence offer no indication as to the nature of the chemical mechanism of nitrogen fixation (6); it has been definitely established that calcium and iron are required in the mechanism of fixation (7, 9); the active growth-stimulating fraction of natural soil humic acid is the iron impurity contained in highly available form, and which under some conditions is capable of supplying the iron required in the mechanism of fixation (9); the first step in nitrogen fixation has been shown to be enzymic in nature, the dissociation constant of the enzyme with respect to nitrogen, the heat of dissociation, and the free energy of dissociation having been determined (8); the over-all process of nitrogen fixation from nitrogen gas to protein has been shown to be rather highly efficient, thermodynamically (4).

ACKNOWLEDGMENT

The writers wish to express appreciation for the material cooperation of F. G. Cottrell and C. H. Kunsman in the preparation of this paper.

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RECEIVED September 12, 1931.

Microanalytical Methods as Time and Labor Savers

E. M. CHAMOT, *Cornell University, Ithaca, N. Y.*

NEITHER microchemical analysis nor chemical microscopy can be considered, as new tools. They are new only in the sense that they are now attracting far more attention than when they were first devised and most chemists are beginning to view them from a somewhat different angle. In these methods we find new systems of procedure rather than new tools.

American chemists have, for the most part, been slow to recognize the value of microanalytical methods because they have regarded them merely as a means for dealing with amounts of material far too small to be handled by the ordinary methods of analysis and have failed to perceive that this very fact—ability to deal with small weights and small volumes—can be taken advantage of and a mode of procedure devised whereby chemical operations can be greatly expedited.

Since the weights and the volumes of reacting compounds are reduced to a minimum, the sizes of the utensils required for carrying on the various operations are correspondingly reduced and the space necessary for a set-up is small indeed compared with that which is essential when standard methods are employed. It follows that time and labor are saved and costs greatly diminished. The economies which can thus be brought about are often of a startling nature, especially where rare and expensive materials or reagents are involved or when the preparation of a suitable sample is a time-consuming task. Many industries are finding that the adoption of microchemical methods results in the saving of days of time and many thousands of dollars.

When comprehensive microscopical methods are combined with microchemical methods, still further economies can be effected. In addition, the increased safety to the analyst of explosives and to the chemist dealing with dangerous reactions is an inestimable advantage.

We now have available, of American manufacture, satisfactory and accurate microbalances and chemical microscopes, and tiny utensils are procurable for all analytical operations. We can carry out with commercially available apparatus practically any chemical operation on a "micro" scale. Moreover, most of the utensils required can be made by any worker

THE MICROCHEMICAL and microscopical methods of analysis which are being developed possess such potential economic possibilities that all analysts should become familiar with them, not only because they provide means for the solution of many problems which cannot be solved by other methods, but also because they provide the most practicable way of reducing costs and of saving time in analytical and research laboratories.

with moderate manipulative ability.

For the information of those who have not yet looked into the merits of microanalytical methods, it can be asserted that substantially all standard methods of quantitative analysis can be so modified as to be made applicable to the analysis of very small amounts of material with no appreciable increase in error.

What is essential, however, is

that the analyst must be a good manipulator and have dexterity and patience as well as steady nerves. In other words, he must be a good analyst. Handling the delicate, fragile utensils and apparatus and supersensitive instruments is no job for a clumsy, careless, or impatient chemist. There is nothing inherently difficult in these methods and nothing which should bar them from any well-conducted laboratory, for the requisite manipulative technic is easily acquired.

Microquantitative methods are available for inorganic as well as for organic compounds (2-5), although the latter appear to be receiving more attention, probably because of Pregl's work and the fact that his book has been translated into English and is therefore well known, whereas the contributions of Emich, Donau, and others in the field of inorganic microanalysis (2-5) are overlooked.

The errors alleged to be inherent in micro-sampling are of no greater relative magnitude than those to be found in our macroscopic methods. If the sampling is performed under a low-power microscope—e. g., Greenough type—the accuracy is certainly in favor of the micromethods, for the microscope is almost certain to reveal any non-homogeneity in the material in question. Moreover, because of the rapidity with which analyses can be made and their very low costs, more samples can be analyzed in less time and there is less temptation to shirk. Thus any errors in sampling and any non-uniformity in the material are more likely to be brought to light.

The development of microanalytical methods to supplement most, if not all, our routine analyses is greatly to be desired, not only because expenses are cut down, but also because more analytical data will be secured, and all with the expenditure of less time and less labor.

These microanalytical methods differ from our so-called standard methods of quantitative analysis in substantially one particular only—they deal with very small amounts of material. The basic principles involved and the reagents employed are the same as when large samples are treated.

It is coming to be generally accepted that the term "microchemical" should be restricted to methods in which about 10 mg. of sample are treated and a microbalance employed. When the weight of the sample approximates 50 mg., the method becomes "semi-micro," and an ordinary sensitive analytical balance can be employed. These semi-micro-methods are especially well suited to industrial control laboratories where speed is essential and the lowering of costs desirable.

ADVANTAGES OF MICROSCOPICAL QUANTITATIVE ANALYSIS

But there is a phase of microanalysis in which our procedures are radically different from those which we term chemical methods. This is a field quite apart and one which is sadly neglected. I refer to microscopical quantitative analysis (1, 6, 8).

While I recognize the importance of microchemical analyses and can fully appraise their value both in industry and in research, I am nevertheless firmly convinced that microscopical methods offer even greater possibilities in the matter of time- and labor-saving. Any competent analyst trained in the use of the microscope can devise new procedures, new tests, and new applications for chemical microscopy.

Chemical-microscopical methods are applicable to syntheses as well as analytical studies. In the former cases, the rate of formation and change of character or the transformation of a compound can often be followed, and much new light can thus be thrown upon a process and possibilities of improvement revealed, facts which could not readily have been brought to light by other means. Studies of relative solubilities are best made with the microscope. Neither high magnifications nor elaborate instruments are essential for the study of the great majority of problems arising in chemical laboratories.

Unlike those methods which we have considered above and which are of general applicability, microscopical quantitative analyses are restricted to certain specific types of material. They were originally devised to enable the analyst to determine the probable percentage composition of materials not susceptible of analysis by ordinary chemical methods—for example, mixtures of starches, meals, crude drugs, paper pulps, textile fibers, rocks, etc. They are by no means restricted, however, to such materials, and are now being applied with great success to ceramic materials, cements, mortars, mixtures of powdered minerals and ores, percussion powders and other explosives, alloys, etc. That is, their special field is the analysis of heterogeneous mixtures of materials of complex chemical composition.

Microscopical quantitative analyses can be successfully applied to any materials provided the following requirements are met:

1. The components of the mixture must differ sufficiently in appearance to permit easy recognition under the microscope or must be susceptible of being rendered different.
2. The different components must bear a reasonably constant relationship to the physical and chemical properties.
3. The specific gravities of the components must be nearly the same or must be known.
4. The sample must be representative of the material.

In general but little preparation of the sample is required when it is in the form of a powder. The chief difficulty lies in obtaining a uniform distribution of the particles in a suitable mounting medium upon an object slide. Alloys must be

surfaced and etched. Fragmental materials can be embedded and sectioned or surfaced.

The ratios of components are determined by comparison with standards, by counts of particles, by the sum of the intercepts along a given line across the field of the microscope, by the use of a reference substance, or by measuring the areas of the different fragments in a suitably prepared section.

The counting of the different components is greatly facilitated by judicious selection of a mounting medium of the proper refractive index, or by counts or comparisons made between crossed nicols.

Microscopical methods of quantitative analysis are worthy of far more attention of chemists than they have received, for in the majority of cases these methods are capable of yielding results with great rapidity and at substantially no cost for reagents and with the expenditure of but little labor. But the analyst must acquire the requisite microscopical technique and learn to illuminate his preparations properly and interpret the images which he sees when looking into his microscope, images obtained with polarized light or with ultraviolet light, as well as with ordinary light.

PREVALENCE OF MICROSCOPICAL QUALITATIVE ANALYSIS

Microscopical qualitative analysis no longer requires any propaganda in its behalf, for it has come to be accepted in most laboratories as a most welcome substitute for the less rapid, less easily interpreted and far more costly chemical methods.

Although the recognition of cations and anions is a comparatively simple matter, the identification of compounds usually calls for a rather comprehensive knowledge of optical crystallography, a knowledge which unfortunately is seldom acquired by the chemist. This, in a way, is a new tool for the chemist and it is quite important that he possess it if he is to make full use of the polarizing microscope in the solution of the intricate problems arising in his investigations. This is especially true if his field is organic chemistry or in the border-land between chemistry and biology.

The application of the micromanipulator in chemical microscopy (7) opens up untold possibilities in the analysis of substances present in such minute quantities as to be invisible to the naked eye. The time has come when it is no longer necessary that material to be analyzed must be visible to the eye. If it can be rendered visible under the microscope, the probabilities are that it can be analyzed.

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Magneto-Optic Method of Analysis as a New Research Tool

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THE MAGNETO-OPTIC method of analysis, which has been in the experimental stage for the past four years, has yielded results in the study of compounds in solution which indicate that it should be found of value in certain problems related to the following lines of research:

1. *Qualitative analysis, particularly in cases of extremely small amounts of materials.*

2. *Quantitative analysis, with an accuracy under best conditions of two to three significant figures. Some advantages of the method are sensitivity of the order of 1 part in 10^{11} ; non-interference of other substances present; and the fact that the sample is unaffected by the analysis.*

3. *The study of isotopes. The number of the characteristic minima of light intensity is, with few*

exceptions, the same as the number of known isotopes of the metallic element of the compound. The minima make their threshold appearances, in general, in the order of the abundances of the various isotopes of the metal as the concentration of the solution is increased. Results of interest have very recently been obtained from an investigation of leads of ordinary and of radioactive sources. Evidence of two isotopes of hydrogen is cited.

4. *The detection of intermediate compounds in certain reactions.*

While the method has been applied chiefly to analyses of solutions of inorganic compounds, a limited amount of investigation has shown that it has approximately the same sensitivity for organic compounds.

TWO very surprising observations made during the course of experiments (1, 5) having to do with the measurements of differential time lags of the Faraday effect in liquids suggested a new means of chemical analysis. These observations were, first, that two or more substances mixed together retain their individual time lags—that is, produce at definite points of the scale their characteristic minima of light intensity, unaffected by the presence of other substances; and second, that a minimum which is characteristic of any compound persists until the concentration of the compound is reduced to about 1 part in 10^{11} . These experimental results through the investigations of the last few years have been found to hold for a wide range of inorganic compounds. The same results have been obtained for the limited number of organic substances which have been examined. In no case has an exception been met with. There was early revealed a relationship pertaining to inorganic materials in solution, which has contributed immeasurably to the effectiveness of the method as a tool for analysis. The reference is to the functional dependence, the nature of which is still not known with accuracy, between chemical equivalents and scale readings (or differential time lags). Meager studies of organic compounds have not yet disclosed a corresponding relationship for these substances. The remarks in this paper will be confined exclusively to the method as applied to inorganic compounds.

Figure 1 is a diagram of the apparatus and connections. Detailed description of the principles and manipulations has been published elsewhere (1), which for lack of time cannot be repeated here. Light from the spark G (usually the $Mg4481A$ line) passes through the optical train consisting of the lens L , slit S , color filter F , the Nicol prism N_1 , cells containing the liquids in the helices B_1 and B_2 , and finally the Nicol N_2 , to the eye (or the photoelectric cell), E . The trolley system T_1T_1' and T_2T_2' has an effective length of about 20 meters, along which extends the wire-path scale laid off in units corresponding to the speed of light. A short light-path scale is mounted between B_1 and N_2 , along which B_2 is displaced in locating minima when, on account of the closeness of the minima, it becomes necessary to em-

ploy a combination of the wire-path and the light-path scales. The discharge of the condenser C causes current surges to traverse the helices B_1 and B_2 , establishing and relaxing the opposing magnetic fields to which the liquids are subjected. A variety of ways of charging C have been employed with success, the positions of the minima being unchanged with such variations. The scheme outlined in the diagram has proven most satisfactory. P_1 and P_2 represent the high-tension and filament transformers, respectively, R_1 and R_2 sliding rheostats, K the Kenotron rectifying tube, and H_1 and H_2 inductances which may be used or omitted depending upon the character of the set-up.

The method becomes a tool for making analyses after one has established the scale readings of minima for the series of compounds in which he is interested. Since the wire-path scale is always employed, either alone or in conjunction with a short light-path scale, the positions of minima on the scales of different set-ups are not necessarily in exact agreement. Four different magneto-optic devices have been constructed at the Alabama Polytechnic Institute, in different rooms and in different buildings. The divergence between scale readings on two different devices is usually not more than a few millimeters, except toward the extreme ends of the scale, where it becomes somewhat greater. The only safe precaution is to calibrate each new scale, using known compounds of the highest purity available and concentrations around 1 part in 10^{11} in order to reduce the likelihood of mistaking some impurity for the compound in question. The determination of the scale readings of a new series is a very laborious undertaking. It is a fatiguing process even to experienced observers, especially if engaged in for many hours a day. Once the scale readings are determined with precision, the analyses may be carried out with more ease and rapidity. No one, however, should expect to become proficient in this work until he has visited a laboratory where the method is in operation and where he may test his ability to read the minima with dependability by making analyses of some (to him) unknown solutions. Every eye is not adapted to this type of observation.

Some months ago, Christensen, Waldo, and the author

(2) succeeded in building a photoelectric-cell circuit sufficiently sensitive to replace the eye in reading minima. During the past summer some added refinements in the photo-cell arrangement have been introduced and the prospects are promising for still further improvements. The photoelectric compared with the visual method is very slow and tedious, because of the difficulties involved in controlling adjustments in a circuit where variations in a minute unidi-

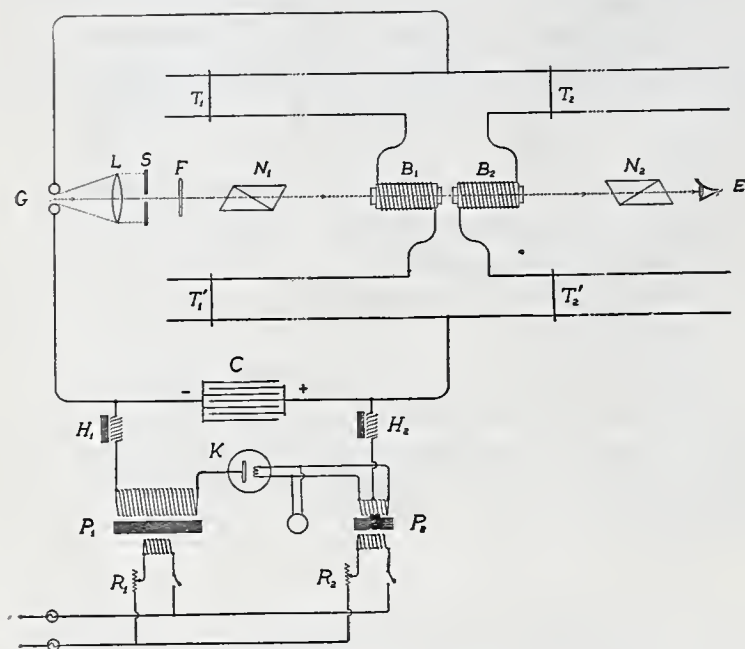


FIGURE 1. MAGNETO-OPTIC APPARATUS

rectional current must be indicated. When satisfactory adjustments were obtained, work would usually be carried on well through the night, as the cell circuit, after standing idle for a day or more, would ordinarily entail the loss of considerable time spent in readjustments when used again. More recently some of these difficulties have been surmounted. The chief interest in using the cell has been centered in checking and confirming the previous visual observations. Thus far there has been complete accord with the results obtained visually. The cell in its present stage of development cannot be recommended as a competitor of the eye, on account of the far greater speed and ease with which the latter can do analyses.

The scale readings of a very extensive series of chlorides (of more than fifty metals) and of a fairly extensive series of nitrates, sulfates, and hydroxides, most of which have been published (5), have been determined. In Figure 2 these data are exhibited in graphical form. The curves are representative of the results for chemical equivalents up to 100 or thereabout, beyond which they fail to conform to the data. One notable exception, however, is that of cadmium chloride and sulfate, minima of both compounds falling seven or eight chemical-equivalent units above their respective curves. The minima for a representative number of all the halides of the lighter metals have also been read and published (6), and the work on phosphates, pyrophosphates, and carbonates is under way. In each of these series the results thus far obtained show a functional relation between chemical equivalent and scale reading quite similar to that which holds for the series in Figures 2 and 3, and they yield the same types of curves. With one of these

curves at hand, one can predict with certainty the region of the scale in which will appear the minima of any compounds of the series. There is overlapping in some instances, however, particularly in the heavy metals with several isotopes and in those whose atomic masses differ but slightly.

This so-called magneto-optic method, which has been in the experimental stage for the past four years, has yielded results in the study of compounds in solution which indicate that it should have a value in certain problems related, directly or indirectly, to the following lines of research.

QUALITATIVE ANALYSIS

The method lends itself readily and conveniently to purely qualitative analysis. Its great sensitivity is likely to be objectionable in analyses of the more common and abundant elements, unless proper precautions are taken to prevent their introduction into the vessels as contaminations. Since the minima appear both to the eye and to the photoelectric cell with nearly the same distinctness in all concentrations ranging approximately from 1 part in 10^{11} to 1 part in 10^2 , it is obvious that impurities are scarcely distinguishable from the predominating constituents of the solution. The method is therefore not recommended for ordinary qualitative analysis. It should, however, prove of considerable service in the analysis of the rare elements and also of the more common elements when they are present in traces only, as, for example, in the occurrence of certain metals in foods. It was entirely by this method that evidence of the presence of element 87 (3) and later of element 85 (6) was obtained.

The presence of foreign substances causes no interference in the analysis nor is the solution under test affected. Inasmuch as compounds of the metallic elements, instead of the elements themselves, are detected, it is possible to run several checks, where there is doubt of the result or where the importance of the analysis may warrant the added labor. This is done by examining the solutions after the metal has been converted into different compounds, such as the chloride, the sulfate, etc. More commonly, the analysis is confined

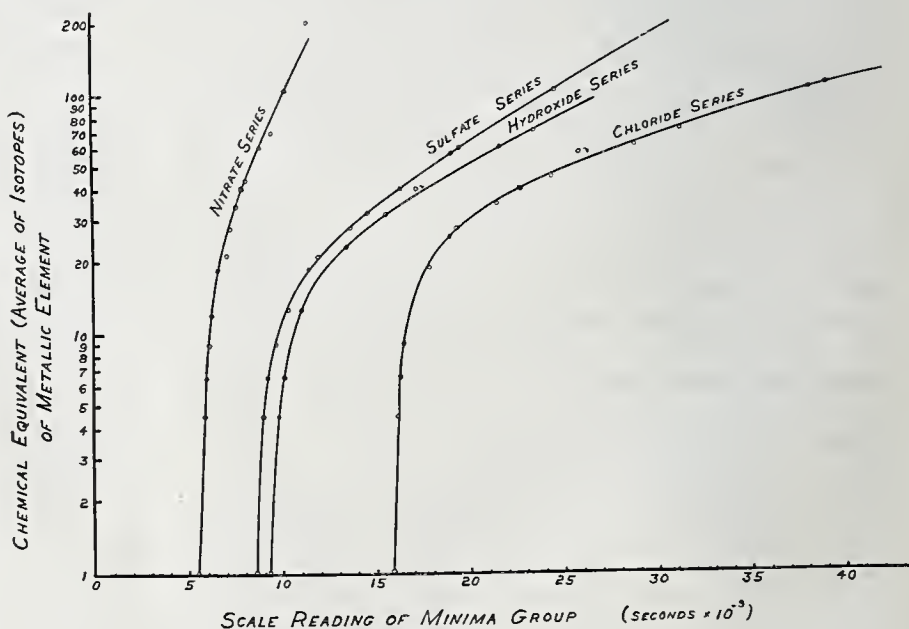


FIGURE 2. CHLORIDE, NITRATE, SULFATE, AND HYDROXIDE SERIES

to but one compound and the chloride is preferred because of the wide scale spacings of the chloride minima.

QUANTITATIVE ANALYSIS

In order to obtain quantitative results one must first determine the sensitivity of the method for the given com-

pound. This is done by preparing a series of concentrations down to 1 part in 10^{12} , or less, in which the characteristic minima are not visible, and then by gradually increasing the concentration until the minima make their definite threshold appearances. The sensitivity for practically all compounds for which it has been determined is several parts in 10^{12} . The unknown solution is examined in the same manner in a series of increasing concentrations until the first appearance of the minima is noted. Under best conditions it is possible to attain an accuracy of two to three significant figures. Further work must be done before the limits of accuracy can be more definitely set. Quantitative work imposes unusually severe demands upon the observer because of the difficulty in judging at what concentration the minima, at first very indistinct, definitely come in. Much practice is required. There has not yet been opportunity to ascertain to what accuracy the photoelectric cell will give quantitative results.

STUDY OF ISOTOPES

The belief that the magneto-optic method detects isotopes and therefore provides a new approach to problems in isotopy is based upon several considerations. The number of minima, with few exceptions, is the same as the number of known isotopes of the metallic element. This is true regardless of the particular compound in which the metal exists, more than 140 such compounds having been examined. One would expect each isotope to produce a minimum, in consequence of the relationship which subsists between atomic mass and scale reading. The differential time lags of the isotopes of a given element, however, appear to vary directly, rather than inversely, with the atomic masses of the individual isotopes (4). The exceptions in the agreement between the number of minima and the number of isotopes referred to, are: lead, number of minima, 4, number of isotopes reported, 3; barium, number of minima, 4, number of isotopes reported, 3; zinc, number of minima, 4, number of isotopes reported, 7; hydrogen (in acids and water), number of minima, 2, number of isotopes reported, none. Zinc compounds are to be rechecked more carefully in search of additional, closely adjacent minima. It is believed that the number of minima for lead and barium represent the number of isotopes of these elements, though there is always the possibility of being misled by an impurity.

A most interesting case is presented in what appears to be the minima produced by hydrogen as it occurs in all the inorganic acids dealt with and also in water, in each of which there are consistently two minima (5, 6). Because of their closeness the two minima of water until recently had been observed as one. The acids are nitric, sulfuric, phosphoric, pyrophosphoric, carbonic, and all the halogen acids. The data are displayed graphically in the two curves of Figure 3, in which the combining equivalent of the negative radical is plotted against the scale reading. These results would be in accord with those of other metals if two isotopes of hydrogen are postulated. Quantitative experiments recently carried out on these acids and water, interpreted upon this postulate, indicate without exception that the lighter isotope is far more abundant, very roughly in the ratio of several thousand to one, and further, that, judged from the closeness of the two minima, the mass of the heavier isotope is probably 2, though the evidence as to the exact mass is not conclusive. There seems to be no explanation of these

doublets unless it be upon the hypothesis of two isotopic components of hydrogen.

The minima make their threshold appearances, in general, in the order of the abundances of the various isotopes of the metal as the concentration of the solution is increased. This is also confirmed by the photoelectric cell in that the magnitudes of the galvanometer deflections are greater for the minima which correspond to the more abundant isotopes, a solution of any convenient concentration being used. The numerical ratio of the abundance of the isotopes as given by this method, however, is not in harmony with that sup-

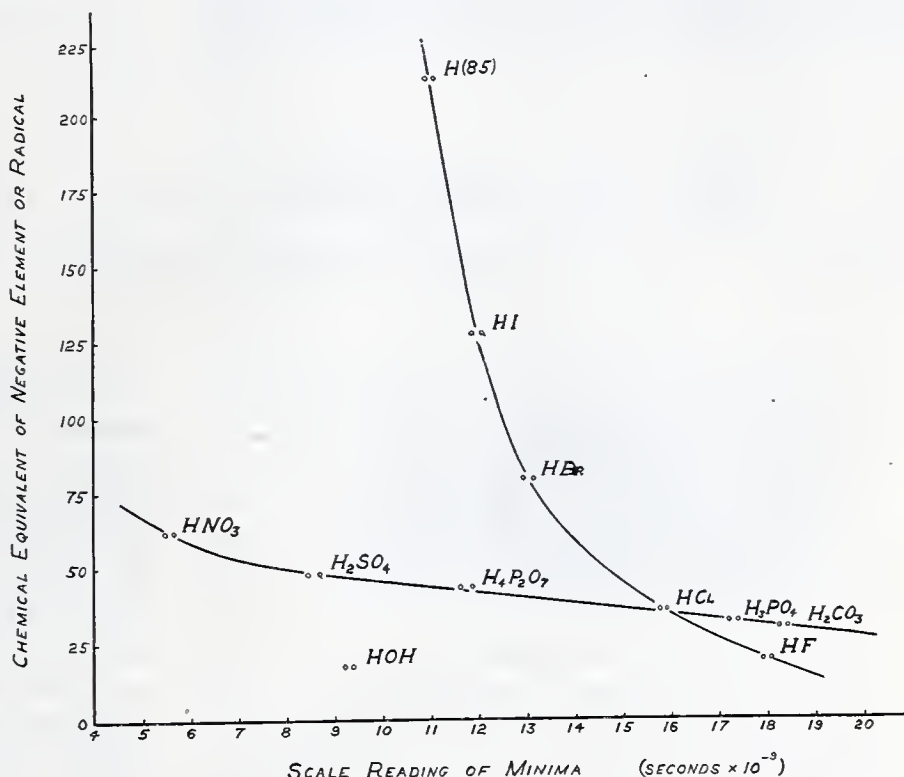


FIGURE 3. HYDROGEN SERIES

plied by other methods. A very much smaller ratio is uniformly obtained as though the isotopes exert upon each other some mutual influence whereby the less abundant atoms are in some way induced by their isotopic neighbors to respond more energetically to the magnetic field. There is no satisfactory explanation for this discrepancy, but it is believed that it may have an important bearing upon other problems connected with the theory of solutions. There is one striking exception, ordinary lead, in which approximately the same proportions of three isotopes are found as Aston reports. An additional minimum indicative of a fourth isotope of lead, least abundant of them all and of atomic mass 205 or less, is present.

During the present summer in this laboratory, Edna R. Bishop and Margaret Lawrenz of the Alabama Experiment Station research staff have subjected the magneto-optic method to a rather thoroughgoing test as a tool for the quantitative study of isotopes. Their unpublished findings on ordinary lead, to which reference was made in the foregoing paragraph, and those on uranium and thorium leads, afford one of the most conclusive proofs that the different isotopes are singled out in the order of their abundance. In uranium and thorium leads, nature favors us with separated isotopes. In uranium salts, there is found only the minimum appropriate to lead 206, and in thorium salts only the minimum appropriate to lead 208. Other unpublished data which they are accumulating concern the question of the selective absorption of different isotopes of an element by plants, a problem in which the method is finding an interesting and unique application.

OTHER SUGGESTED APPLICATIONS

The method, it would seem, is admirably adapted to the study of slow chemical changes with time and to the detection of intermediate compounds in certain chemical reactions. The author has not had occasion, however, to do work of this character, although one such experiment is under way at present.

Other possible uses of the method than those mentioned no doubt suggest themselves. There is certainly a need for more trained workers in order that the usefulness of this method as a research tool may be still more definitely determined and in order that there may be developed further

improvements that will render the procedure less difficult for the observer both visually and photoelectrically.

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The Ultracentrifuge and Its Field of Research

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THE ULTRACENTRIFUGE was developed to provide a means for accurately characterizing the distribution of particle size in many natural and synthetic substances. Two types of centrifuge are described, one for yielding moderate forces up to 10,000 times that of gravity and the other capable of producing an action 100,000 times that of gravity.

The most important features of ultracentrifugal analysis developed up to the present are: First, the possibility of deciding whether a substance is mono- or polydisperse and, if polydisperse, the range of particle sizes or number of molecular species pres-

ent; second, the uncovering of structural relationships as evidenced by the classification of many proteins into groups which are integral multiples of a molecular weight of 34,500; third, the separation and optical analysis of mixtures of micelles; fourth, the study of the effect of pH on the molecular condition or aggregation of a substance; fifth, the determination of the molecular weights of complex dyes, which opens the way to a study of indicator action and the effect of salts on association; and sixth, the study of the formation of primary colloidal particles and the factors influencing the subsequent growth.

DURING the last fifteen years, and especially the last five, there has come a realization of the importance of an accurate characterization of the distribution of particle size in many naturally occurring materials and synthetic substances designated as macromolecular compounds by the organic chemist, or as lyophilic colloids by the colloid chemist. Many methods have been used to gain a knowledge of particle size, but few have given more than an estimate of the mean size present, and most of them have failed to yield satisfactory answers to certain basic problems under investigation in different fields of chemistry. The biochemist and the medical man would like to ascertain the size of the unit present in filterable viruses and in the bacteriophages. They would also like to know whether a rigorously purified protein has changed its aggregation as a result of the process. The cellulose chemist wonders whether the cellulose molecule changes in size when treated with chemical reagents, or whether the reactions are mainly topochemical. The rubber chemist would like to obtain information on the differences in polymerization of rubber, balata, and gutta-percha, and to decide whether viscosity changes produced by aging or oxidation reflect changes in micellar size. The process of formation of primary particles and subsequent growth and aggregation forms an important phase of colloid chemistry which has hitherto been difficult of attack. The indicator reaction of dyes may be either a structural change or a change in molecular size. The setting of a paint film is supposed to be a colloidal process with the production of high polymers.

THE ULTRACENTRIFUGE

The development and refinement of the ultracentrifuge by Svedberg and his associates (12) have provided a group of methods for answering such questions. Furthermore, these methods promise to avoid many of the weaknesses of the earlier methods and to constitute the most reliable and adaptable technic for investigating dispersity in colloidal solutions.

PRINCIPLES INVOLVED

The principle of the ultracentrifuge is illustrated in Figure 1. A transparent cell containing the solution or suspension to be studied is rotated at a speed sufficient to produce a centrifugal force 1000 to 100,000 times that of gravity. A beam of light passes up through the cell and permits the colorimetric determination, either by visual examination or by photographic recording, of the changes undergone by the solution while the centrifuge is in action. If the solution contains equal-sized particles and the centrifuging is rapid enough, a sharp boundary moves outward. The particle size can then be determined by measuring the displacement of the boundary x_2-x_1 in the time interval t_2-t_1 , and applying a modified form of Stokes' law. With nonuniform material, however, a partial separation is effected, giving one an opportunity to determine the distribution of sizes present from an analysis of the radial variation in concentration (22).

From the molecular-kinetic standpoint there is no distinction between a colloidal particle and a molecule in solution (2). The kinetic energy of any suspended unit which

retains its identity is the same as that of a molecule; therefore, the term "micellar weight" will be used as a generic name for the weight of either a suspended particle or a molecule in solution. "Particle size" will be used to designate the equivalent radius of the molecule or particle. Depending upon the experimental conditions, micellar weight or particle size

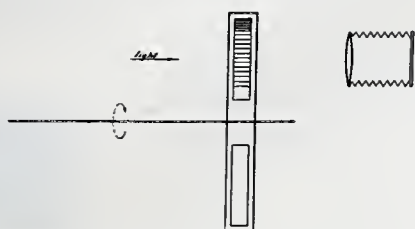


FIGURE 1. PRINCIPLE OF ULTRACENTRIFUGE

may be determined either by the establishment of a sedimentation equilibrium between centrifuging and diffusion or by the measurement of the sedimentation velocity and of the diffusion (13).

REQUIREMENTS FOR SATISFACTORY OPERATION

A centrifuge developing a centrifugal force of 1000 to 10,000 times that of gravity renders possible the study of the sedimentation velocities of the lyophobic inorganic colloids and the sedimentation equilibria of the proteins and other organic lyophilic substances of micellar weight greater than 10,000. For the determination of the sedimentation velocities of these lyophilic substances and for the sedimentation equilibria of most substances in the range 10,000 to 1000, centrifugal forces of about 100,000 times that of gravity are required.

The most important conditions for satisfactory ultracentrifugal analysis are: First, no vibrational or thermal effects should disturb the sedimenting system; second, the

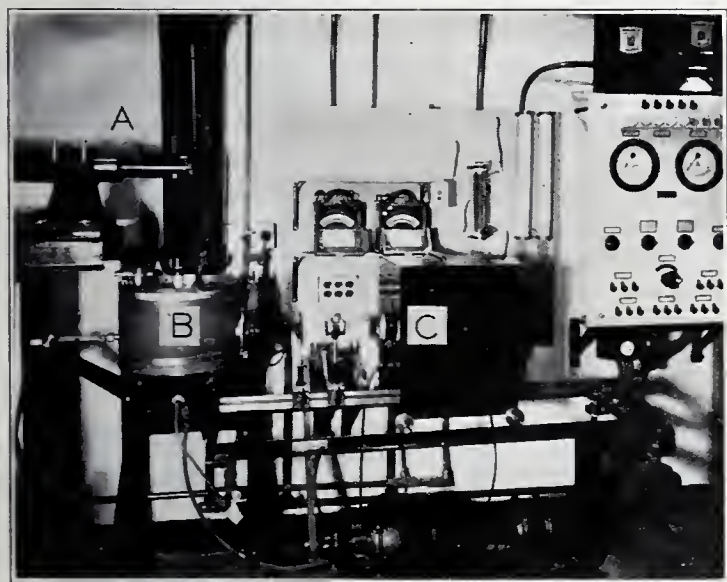


FIGURE 2. PHOTOGRAPHIC REPRESENTATION OF LOW-SPEED ULTRACENTRIFUGE. A, front end of camera; B, centrifuge proper; C, illumination unit

amplitude of vibrations of the rotor must be small enough and the optical system well enough defined that sharp pictures can be obtained; third, cells should be constructed to withstand the pressures of 100 to 200 atmospheres produced when the centrifugal force reaches the magnitude of 100,000 times that of gravity; and fourth, the substance must undergo no deterioration during the centrifuging.

LOW-SPEED TYPE OF ULTRACENTRIFUGE

An improved form of ultracentrifuge used at the du Pont Experimental Station will serve as an example of the machines developed for investigations requiring moderate centrifugal forces (23). This machine was constructed to permit the use of either a colorimetric or a refractive-index method for measuring concentration changes. In some systems, for example, rubber in benzene, cellulose nitrate in acetone, or cellulose in cuprammonium solution, the light-absorption method is not applicable because the absorption coefficient of the dissolved substance is not sufficiently greater than that of the solvent in any usable region of the spectrum. If the solution is not turbid, the index-of-refraction method is more generally applicable because there is more frequently a sufficient difference in the refractive indices of solvent and solute. The method involves the measurement of the displacement of the lines of a micrometer scale photographed through the solution in the centrifuge cell (5, 6). In order to increase the sensitivity of the method and to insure freedom from parallax, a photographic lens of rather long focal length is used—i. e., about a meter and a half.

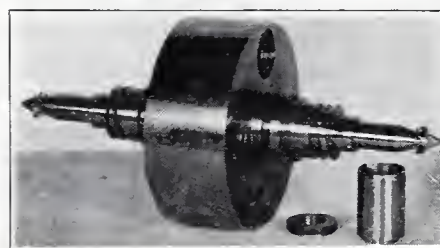


FIGURE 3. ROTOR OF OIL-TURBINE ULTRACENTRIFUGE

A photograph of the arrangement of the centrifuge is shown in Figure 2. The machine is built on the base of a rayon-spinning centrifuge designed by Siemens and Schuckert (3). Any tendency to injurious vibration is immediately counteracted by a rubber ring on which the synchronous motor is supported by means of a wide flange. The speed is regulated by means of a frequency transformer which permits a variation in speed from about 1500 to 12,000 r. p. m. Exposures are made by means of electromagnetically operated shutters. Speed is indicated by means of a magneto connected to the frequency transformer. As in the earlier types of centrifuges, thermostatic control is provided from 0° to 50° or 60° C., and hydrogen or helium is blown through the rotor chamber to cut down frictional heat.

HIGH-SPEED TYPE OF MACHINE

For some purposes, however, it is desirable to have available extremely high centrifugal forces of the order of 100,000 times that of gravity. Then it is possible to determine the sedimentation velocity of lyophilic substances in two or three hours which might require from two to three days to attain sedimentation equilibrium with a low speed. If we are working with unstable materials that change continuously, this is a very decided advantage. It is also possible to obtain more exact information about mixtures of micelles because of the greater separation in the higher centrifugal field.

The oil-turbine type of ultracentrifuge was developed by Svedberg and Lysholm (18, 21) to produce fields of force up to 100,000 times that of gravity and yet not heat injuriously. Figure 3 shows the rotor. Figure 4 gives a diagrammatic representation of the centrifuge. The rotor is made of chrome-nickel steel and has openings for four cells. It is driven by oil under a pressure of twelve atmospheres impinging against two eight-bladed turbines, one at each end

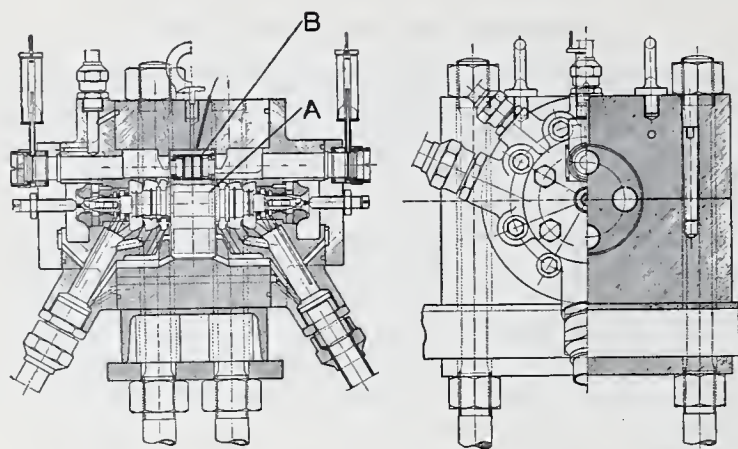


FIGURE 4. CROSS-SECTIONAL VIEW OF OIL-TURBINE ULTRACENTRIFUGE. A, rotor; B, cell

of the shaft. The rotor revolves in hydrogen or helium gas at a reduced pressure. Under optimum conditions the temperature difference between the rotor and the casing is only 1.5° at 40,000 r. p. m. The oil from the bearings is prevented from entering the rotor chamber by an elaborate system of deflectors. The temperature is adjusted by cooling the oil before it is admitted to the turbine chambers. The observation windows are protected from oil mist by electromagnetically controlled shutters. The speed of the rotor is determined by means of a stroboscopic tachometer. The complete optical system and stroboscopic device for measuring the speed of the oil-turbine centrifuge is shown in Figure 5.

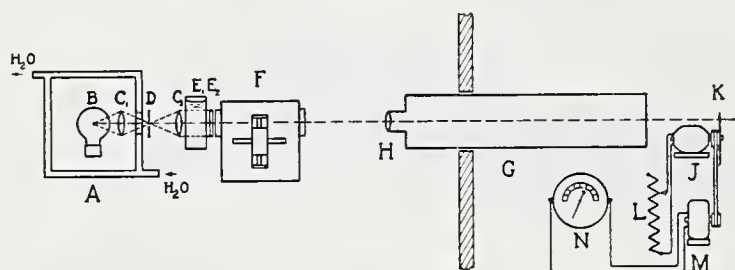


FIGURE 5. OPTICAL SYSTEM FOR OIL-TURBINE ULTRACENTRIFUGE

- | | |
|----------------------------|---|
| A, Water-cooled lamp house | H, Objective |
| B, Lamp or mercury arc | J, Motor |
| C, Water filter | K, Stroboscope disk |
| D, Light filter | L, Resistance |
| E, Shutter | M, Magneto generator |
| F, Centrifuge | N, Hot wire ammeter, readings in r. p. m. |
| G, Camera | |

THEORY

At sedimentation equilibrium the change in free energy, dF , or the change in concentration with time, dc/dt , becomes equal to zero at every point in the cell; integration of the basic differential equations give the following relations for micellar weight (20):

$$M = \frac{2RT \ln \left(\frac{c_2}{c_1} \right)}{(1 - V\rho) \omega^2 (x_2^2 - x_1^2)} \quad (1)$$

For particle size the relation is

$$r = \sqrt[3]{\frac{3RT \ln \frac{c_2}{c_1}}{2N\pi(\rho_p - \rho_m)\omega^2(x_2^2 - x_1^2)}} \quad (1a)$$

where M is the micellar weight, r the effective radius of the particle considered as a sphere, R the gas constant, 83.2×10^6 , T the absolute temperature, N the Avogadro number, V the partial specific volume of the substance, ρ the density of

the solution, ρ_p the density of the particle, ρ_m the density of the solvent, ω the angular velocity, and c_2 and c_1 the concentrations at the points x_2 and x_1 distant from the axis of rotation of the centrifuge. The concentration is determined by the light-absorption method or in terms of the refractive index by Lamm's method (6). No assumptions have been made in Equation 1 as to form and structure of the molecule or particle. In addition, there are no membrane complications as in the osmotic-pressure method of determining micellar weight, and the presence of electrolytes is beneficial rather than harmful in that electrical potentials due to the separation of electrical charges having different mobilities are repressed.

On the assumption that the frictional force per mole is the same for sedimentation and for diffusion, the following simple sedimentation-velocity equations for small x -intervals are obtained (20):

$$M = \frac{RTs}{(1 - V\rho)D} \quad (2)$$

or

$$r = \sqrt{\frac{9\eta s}{2(\rho_p - \rho_m)}} \quad (2a)$$

Both D , the diffusion constant, and s , the sedimentation constant ($1/\omega^2 x \cdot dx/dt$), characteristic of each molecular species or particle size, are calculated directly from the data obtained during the centrifuging (21).

FIELD OF RESEARCH

In order to give a concrete idea of the range of problems to which the ultracentrifuge technic has been applied, a number of examples are given to illustrate some of the salient features. Many of the illustrations are drawn from the protein investigations carried out by Svedberg and co-workers (12, 14), and the others from work carried out at the du Pont Experimental Station. The technic of study brought out in the examples drawn from the protein work should be considered as of equal applicability to the whole field of natural and synthetic polymers and colloidal material. Other phenomena which can be studied by means of the ultracentrifugal methods, such as thermodynamic and molecular-kinetic properties of large molecules, and certain chemical and physical problems have been collected in an earlier paper (9).

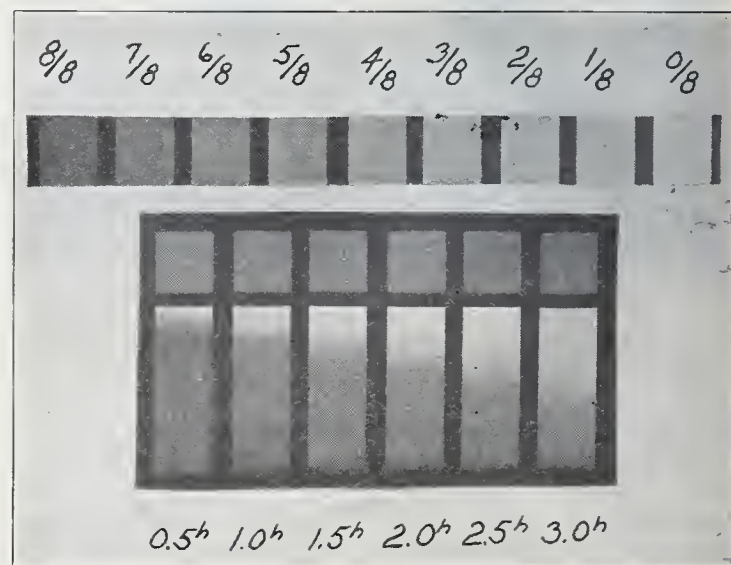


FIGURE 7. SEDIMENTATION OF CARBON MONOXIDE-HEMOGLOBIN

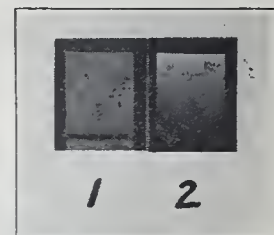


FIGURE 6. SEDIMENTATION EQUILIBRIUM OF HEMLOCK EXTRACT

To illustrate the appearance of a sedimentation equilibrium, Figure 6 is reproduced. It refers to a centrifuging carried out on a 2.74 per cent solution of hemlock extract at a centrifugal force approximately 7500 times that of gravity, with the use of the strong absorption of the material in the blue region of the spectrum for the photographic determination of concentration. Exposure 1 represents the start of the

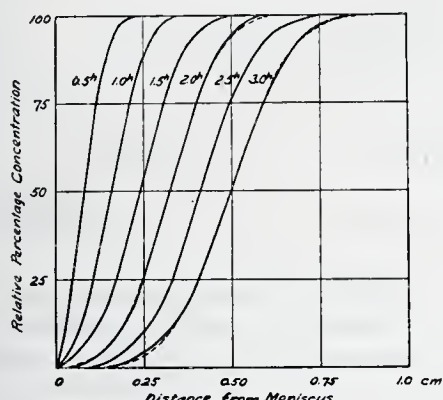


FIGURE 8. SEDIMENTATION CURVES OF CARBON MONOXIDE-HEMOGLOBIN

centrifuging, and exposure 2 the final equilibrium state 44.5 hours after the start. A value of approximately 10,000 was obtained for the micellar weight of this tannin body. The red coloring matter of the extract was found to be either an integral part of the micelle or so strongly adsorbed as to appear to be.

As an example of the sedimentation-velocity method, Figure 7 gives a reproduction of the photographic record of the centrifuging of a 1 per cent solution of carbon monoxide-hemoglobin subjected to a field of force 87,000 times that of gravity. It shows the sedimentation of the solution 0.5, 1.0, ... 3 hours after the start of the run. The top row is the scale of concentrations in fractions of 1 per cent.

MONODISPERSE SUBSTANCES—HEMOGLOBIN

By means of the ultracentrifuge it is possible to ascertain whether a substance exists as a single molecular species or is made up of several. Figure 8 gives the variation of concentration with distance after 0.5, 1.0, ... 3 hours of centrifuging

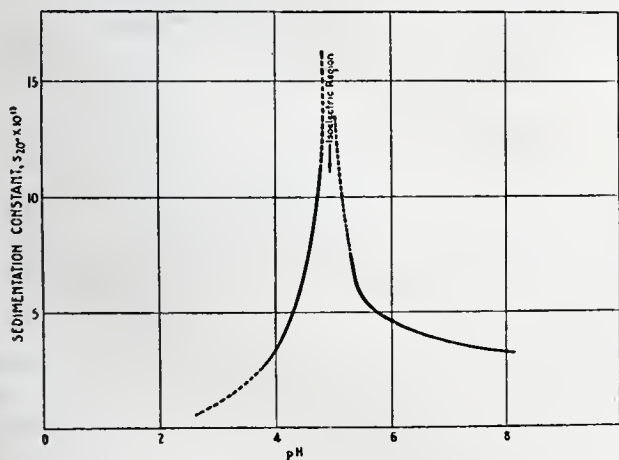


FIGURE 9. VARIATION OF SEDIMENTATION CONSTANT, s , OF GELATIN WITH pH (4)

of carbon monoxide-hemoglobin, a photographic record of which was given in the previous figure (21). The dotted curves for two and three hours represent the theoretical diffusion curves for a substance with a uniform molecular weight of 68,000 subjected to the same experimental conditions; therefore, hemoglobin consists essentially of a single molecular species.

POLYDISPERSE SUBSTANCES—GELATIN

Although many proteins have been found to be monodisperse, such substances as gelatin, gliadin, and muscle globulin are polydisperse and usually are unstable. Krishnamurti (4) found gelatin to contain a range of micellar weights from 10,000 to at least 70,000 at a temperature of 20° C. by the sedimentation-equilibrium method and to show large variations in sedimentation velocity with hydrogen-ion concentration. Figure 9 presents his data on the change of the sedimentation constant of gelatin with pH at 20° C. It is evident that in strongly acid solution the gelatin decomposes to relatively simple molecules in contrast to the action of egg albumin in strongly acid solution (Figure 10). At the

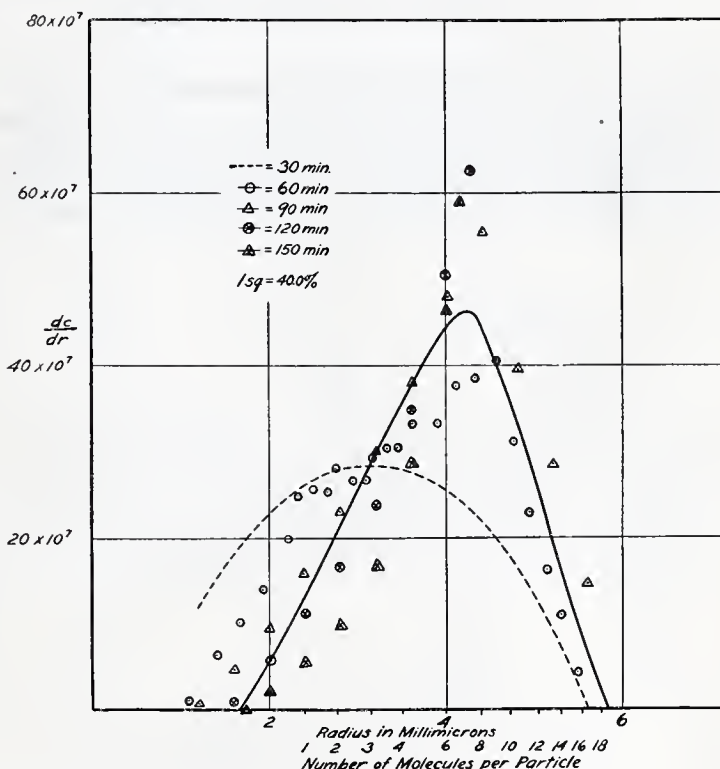


FIGURE 10. DISTRIBUTION CURVE FOR EGG ALBUMIN IN 0.1 N HYDROCHLORIC ACID

isoelectric point the gelatin tends to precipitate out, but in the moderately alkaline region there is practically no aggregation. In contrast to gelatin, egg albumin has the same sedimentation constant over the rather wide pH range of 2.0 to 9.0 (7, 25).

EFFECT OF ACIDS AND ALKALIES ON MICELLES

Many materials undergo large changes when subjected to strong alkalis or acids. For instance, after native cellulose has been steeped in strong alkali or treated with strong acids, the x-ray diagrams are different from that of the native cellulose. Strong acid produces an aggregating effect on egg albumin, in contrast to the decomposition that usually occurs in strongly alkaline solutions of proteins. Figure 10 shows the denaturing action of 0.1 N hydrochloric acid on an originally monodisperse solution of recrystallized egg albumin with a molecular weight of 34,500. The strong acid caused the egg albumin to aggregate to gel clumps containing an average of about seven molecules per particle, which increased in size during the determination (7).

SEPARATION OF MIXTURES OF MICELLES

The relative proportions of mixtures of substances, either similar or divergent in character, may readily be determined. With the ultracentrifuge, efficient separation can be made of

TABLE I. MICELLAR WEIGHTS OF NATURALLY OCCURRING SUBSTANCES (SVEDBERG AND CO-WORKERS) AND MOLECULAR WEIGHTS OF COMPLEX DYES

SUBSTANCE		MICELLAR WEIGHT	APPROXIMATE MULTIPLE
MONODISPERSE PROTEINS			
Class I	Egg albumin, insulin, and Bence-Jones' protein	34,500	1 × 34,500
Class II	Hemoglobin and serum albumin	68,000	2 × 34,500
Class III	Serum globulin	104,000	3 × 34,500
Class IV	Edestin and seven plant globulins	208,000	6 × 34,500
Class V	Hemocyanins	2-5 × 10 ⁶	
POLYDISPERSE PROTEINS			
Casein, lactalbumin, gelatin, muscle globulin, and ten others		Mean micellar weight falls in approx. same range as monodisperse proteins	
CELLULOSE			
Cotton linters		40,000	
Wood		40,000 and smaller	
Viscose (cellulose xanthate)		33,000 (approx.)	
Cellulose nitrate (largely degraded)		10,000 (approx.)	
COMPLEX DYES			
Sodium eosinate (tetrabromofluorescein)		1,389	2 × formula wt.
Sodium erythrosinate (tetraiodofluorescein)		1,682 and larger	ca. 2 × formula wt.

substances which would be difficult to separate by ordinary recrystallization or fractionation procedures. Figure 11 gives an example of such a separation. It shows the concentration gradient plotted against distance along the cell for a mixture of equal parts of serum albumin and edestin investigated by

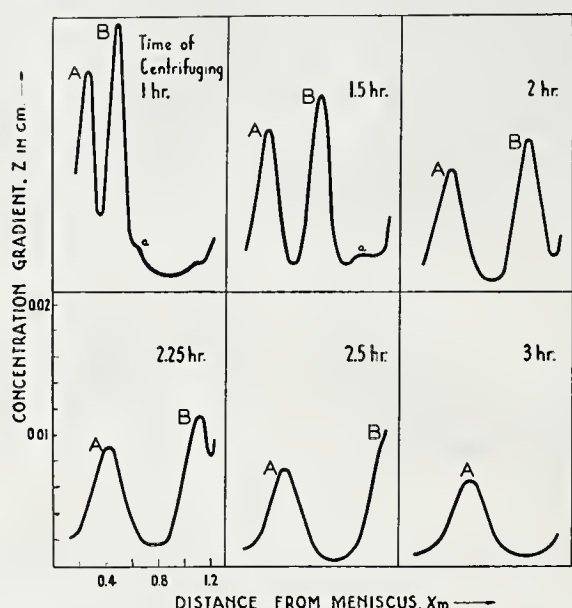


FIGURE 11. SEPARATION OF MIXTURE OF SERUM ALBUMIN AND EDESTIN PRODUCED IN ULTRACENTRIFUGE (5). A, serum albumin, molecular weight, 67,500; B, edestin, molecular weight, 208,000

Lamm (6). The two maxima become more and more separated as the centrifuging progresses. After three hours the edestin has been practically completely removed. Lamm's calculations showed that the movement of the two proteins was nearly but not completely independent of each other.

REGULARITIES IN PROTEIN STRUCTURE

Table I summarizes the regularities observed by Svedberg and his co-workers (12, 14, 11, 8), in the molecular weights of proteins and other complex substances. The micellar weights of the monodisperse native proteins, with the exception of the hemocyanins, fall into classes of one, two, three, and six times 34,500. This rather surprising regularity and others found by Svedberg (15) remained without explanation until some recent considerations put forth by Astbury and Woods (1). They suggest that the sequence of numbers, 1, 2, 3, and 6, may arise from the crystallographic configurations that neighboring peptid chains can assume when linked together by the secondary valences of $-\text{CO}-$ and $-\text{NH}-$ groups. Such molecular associations might be expected to be reversible,

an assumption verified by the experimental findings of Svedberg and his associates (24). Astbury and Woods attempt to explain the fundamental unit of weight by suggesting that the primary-valence chains are limited to a length corresponding to 34,500 owing to vibrational instability.

Svedberg's study of the molecular complexity of insulin (16) would seem to prove that the possibility of synthesizing this hormone is extremely remote

CELLULOSE STUDIES

In his ultracentrifugal investigation of the micellar weight of cellulose in cuprammonium solution, Stamm (11) found that concentrations of cellulose above a few hundredths of a per cent had a marked depressing effect on the values obtained for the diffusion constant and the sedimentation constant, a phenomenon which occurs when some interaction between the micelles occurs or incipient gelling effects arise. In this case it was likely due to the elongated shape of the micelles rather than to their size. The variation of the specific sedimentation velocity and of the diffusion constant with cellulose

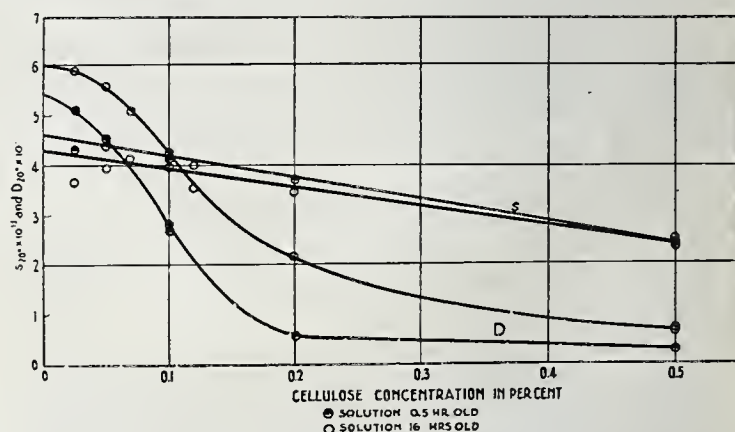


FIGURE 12. VARIATION OF SEDIMENTATION CONSTANT, s , AND OF DIFFUSION CONSTANT, D , WITH CELLULOSE CONCENTRATION (11)

lose concentration is shown in Figure 12, both for solutions centrifuged immediately after preparation and for solutions sixteen hours old. The degradation produced by the exposure to the air during the sixteen-hour period produced very little effect on the sedimentation velocity. However, an appreciable increase in the diffusion constant occurred, caused probably by the formation of a small amount of decomposition products of low molecular weight. Stamm found the micellar weight of cotton linters alpha cellulose (Table I) to be 40,000 on a copper-free basis, whereas wood cellulose contained in addition some micelles 20,000 in weight and a small amount of degraded material. Viscose was found to have a slightly smaller micellar weight than cotton linters alpha cellulose.

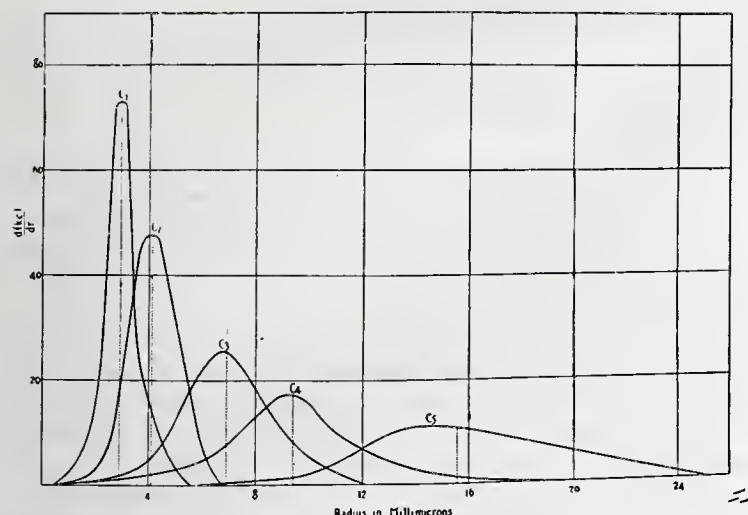


FIGURE 13. WEIGHT-OPTICAL DISTRIBUTION CURVES OF GRADED SERIES OF GOLD SOLS PREPARED BY NUCLEAR METHOD

SOL	MEAN RADIUS	AREA
	<i>mμ</i>	%
C ₁	2.9	108
C ₂	4.1	114
C ₃	6.9	106
C ₄	9.4	96
C ₅	15.6	102

MOLECULAR WEIGHTS OF COMPLEX DYES

It is possible to determine centrifugally the molecular weights of substances of small enough weight to give fairly reliable results by the ordinary methods of physical chemistry. The results obtained from the boiling-point elevation and from the sedimentation equilibrium in a field of force 9000 times that of gravity for the dyes sodium eosinate and erythrosinate agreed rather well (8). The ionization of the dye of course affected both methods. However, the opposing electrical potential arising in the centrifuge from the partial separation of the large dye ions from the small sodium ions may be repressed by the addition of 1 per cent sodium chloride. Under these conditions the dyes were found to consist in solution for the most part of molecules twice the formula weight, with a small amount of more highly associated material for the iodo-compound (Table I).

The successful application of the ultracentrifuge method to the study of these dyes enables us to attack the special problems—degree of uniformity, purity, ionization, and the effect of substituent groups—of substances of molecular weight of the order of 1000 from two converging angles.

FORMATION AND GROWTH OF PARTICLES

The mechanism entering into the formation and growth of colloidal particles forms a rather important phase of colloid chemistry. A graded series of gold sols prepared by successive depositions of gold on the particles of a nuclear gold sol, which contained practically the smallest particles that can exist without re-resolution in a medium, is shown in Figure 13. This series was used by the x-ray laboratory of the station in the analysis of the methods for determining particle size by the broadening of the x-ray diffraction lines. Rinde (10) has studied the various theories of crystal growth in the light of his comprehensive investigations on the variation in the distribution curves of gold sols with conditions of preparation.

When ferric chloride is hydrolyzed at 100° C. the solution first assumes a clear red color but becomes turbid on continued boiling and finally forms a sediment, the rate depending on the original concentration of ferric chloride used. Figure 14 shows the large effect that continued digestion at 100° C. had on an 0.037 *M* ferric chloride solution. The distribution

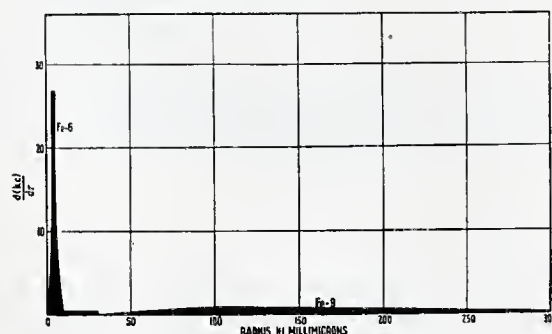


FIGURE 14. EFFECT OF TIME OF HYDROLYSIS ON WEIGHT-OPTICAL DISTRIBUTION CURVES OF FERRIC OXIDE I FROM 0.037 *M* FERRIC CHLORIDE

SAMPLE	TIME OF HYDROLYSIS	MEAN RADIUS	AREA
	Hours	<i>mμ</i>	%
(Fe-6)	1	4.4	90
(Fe-9)	8	132	89

curve of the hydrous ferric oxide formed from one hour's hydrolysis still represents primary particles of 4.4 millimicrons radius. Continued digestion at 100° C. for eight hours gave a coarse, brick-red sediment. The large growth from 4.4 to 132 millimicrons was largely caused by the secondary processes of dehydration and development of crystallinity.

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RECEIVED August 20, 1931. Communication No. 71 from the Experimental Station of E. I. du Pont de Nemours & Company.

Manometers for Low Pressures

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GAGES for measurement of low pressures may be classified in three different groups: (1) direct-reading gages, such as those of the McLeod mercury type; (2) resistance gages, for example, the Pirani-Hale type, which depend upon the change with pressure in heat conductivity of a gas; and (3) ionization gages which involve a measurement of the number of positive ions produced in the residual gas by a definite electron current.

Each of these different types of gages has its limitations and particular field of applications.

The simplest type is the McLeod gage which reads the pressure directly. It does not indicate mercury vapor or water vapor. Manometers based on the radiometer principle, such as that of Knudsen, have not proved convenient for general use, although they are of interest in special investigation; the same remarks apply to viscosity manometers, such as those of Langmuir and others. The vibrating quartz fiber, suggested by Haber and Kerschbaum, and improved by I. Langmuir, has been found useful in a number of cases where it is desired to measure residual pressures of chemically active vapors in sealed-off devices.

As generally useful tools for measurement of low pressures, two types of gages have been developed. The first of these, known as resistance type, makes use of the fact that at low pressures the heat conductivity of a gas is a linear function of the pressure. The gage consists of a tungsten filament mounted in a bulb, and the pressure may be determined by one of three methods:

The filament is maintained at constant voltage, and the change in current measured with change in pressure.

The resistance and, consequently, the temperature of the filament are kept constant and the change in total watts measured.

At constant current the change in resistance is a measure of the pressure.

The temperature of the filament at constant current may also be determined by a thermocouple attached to the filament. With gages of the resistance type, pressures as low as 10^{-5} mm. may be measured quite accurately. The indications vary, of course, with the nature of the gas.

The second type of gage used in high-vacuum technic is known as the ionization manometer and involves a measurement of the ionization produced in a gas by a definite electron current. The electrons emitted from a tungsten or oxide-coated filament are accelerated by applying a positive potential, varying between 100 and 250 volts, to an adjacent electrode (the anode), and the positive ions, resulting from collisions between electrons and gas molecules, are collected by a third electrode (the collector), which is maintained at a negative potential (10 to 50 volts) with respect to the cathode. The ratio of positive ion to electron current is a function of anode voltage and nature of gas, but varies linearly with pressure at the lower range (below 10^{-3} mm.) and is independent of electron current for relatively low values of the latter. On the whole, this type of gage has proved to be the most useful form in high-vacuum work.

RECEIVED September 21, 1931. Presented under title of "New Gages." For more complete discussion of this topic, see *J. Franklin Inst.*, **211**, 689 (1931).

...END OF SYMPOSIUM...

Determination of Isopropyl Alcohol in Ethyl Alcohol

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THE industrial use of mixtures of isopropyl alcohol with ethyl alcohol has given rise to a need for a simple analytical method to determine the proportion of the two alcohols in such mixtures. A method of analysis has been developed on the basis of the difference in the solubility of caustic soda in the two alcohols. The method of analysis is simple and rapid, and accurate to a fraction of 1 per cent of isopropyl alcohol at small concentrations—i. e., less than 20 per cent isopropyl alcohol. Above 50 per cent isopropyl alcohol cannot be determined with any accuracy without diluting the mixture with a known volume of ethyl alcohol to bring the concentration below 50 per cent. The analytical technic involves agitating a sample of the alcohol under question with an excess of caustic soda solution of a standard strength and at a definite temperature. The supernatant alcohol is separated and its alkalinity determined by titration. The alkalinity is referred to as an empirical curve which shows percentage of isopropyl alcohol plotted against alkalinity.

METHOD OF ANALYSIS

A solution of c. p. caustic soda, 410 grams, is dissolved in 1 liter of water. This gives a solution slightly stronger than

30 per cent. The exact strength is determined by titrating with a standard acid solution, and additional water is added until the strength, by titration, is 30 per cent. Samples for titration are weighed.

About 10 cc. of the alcohol mixture in question are taken in a 50-cc. glass-stoppered graduated cylinder. About 20 cc. of exactly 30 per cent caustic soda are added to the alcohol, and the cylinder is placed in a water bath regulated to 25° C. The cylinder is shaken vigorously and then placed in the water bath until the two layers separate completely. The shaking is repeated a second time, returned to the water bath to separate, and then shaken a third time. This procedure insures a minimum time of contact and a minimum time in the water bath, which is necessary to give reproducible results. After the third settling period in the water bath, a sample of the supernatant layer of alcohol is withdrawn in a 1-cc. pipet and titrated with 0.1 *N* sulfuric acid solution using methyl red indicator. The titration volume is referred directly to the graph (Figure 1) for interpretation in terms of 91 per cent isopropyl alcohol present.

In this laboratory a 3-gallon Pyrex battery jar is being used

as a water bath. An initial adjustment of the water temperature is sufficient to complete a given test.

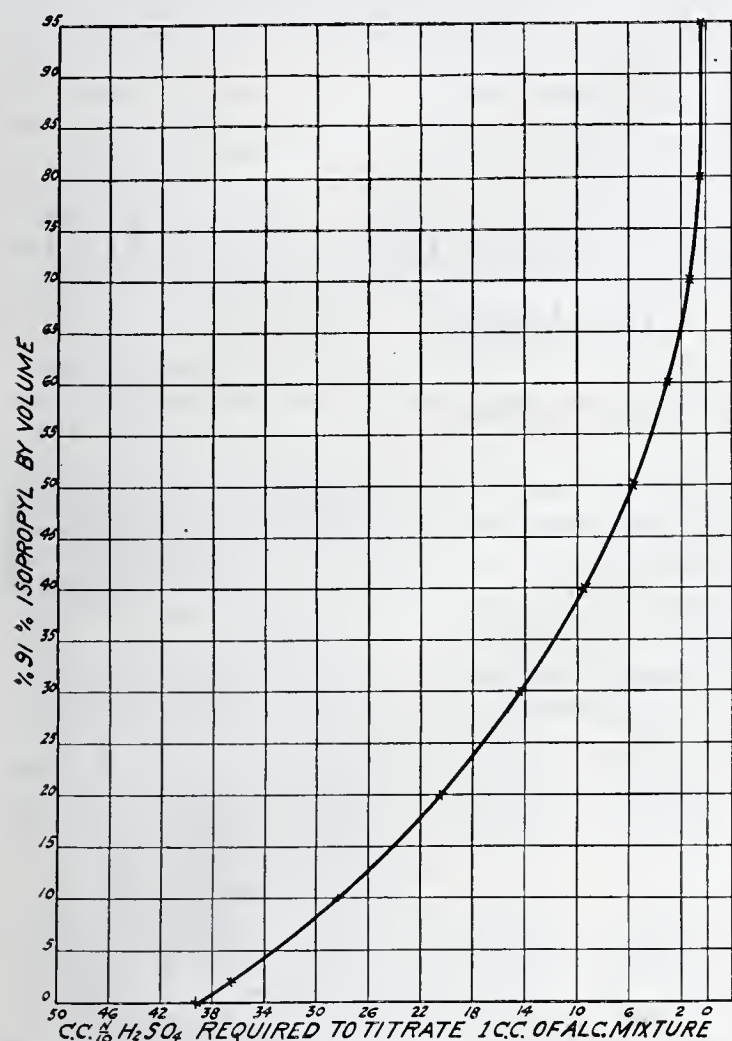


FIGURE 1. ALKALINITY OF ALCOHOL MIXTURES AT EQUILIBRIUM WITH 30 PER CENT CAUSTIC SODA AT 25° C.

The supernatant alcohol is quite free from entrained alkali, as evidenced by the fact that the alkalinity remains unchanged on filtration.

EMPIRICAL RELATION

The graph of Figure 1 expresses the empirical relation between alcohol composition and the solubility of caustic soda in the various compositions. It is the result of experimental work, according to the method described above, on mixtures of alcohol of known composition. These mixtures were made from commercial grades of alcohol, 91 per cent isopropyl and 95 per cent ethyl alcohol (not denatured). Part of the lower range of concentration is plotted to a larger scale and shown as curve C in Figure 2. It can be seen that the method described above gives sufficiently accurate results so that there is no difficulty in drawing a smooth curve through the experimental points. Different operators were able to check points on the curve.

EFFECT OF VARIABLES

The analytical procedure was repeated over the lower range of isopropyl concentration with deliberate variations in one factory at a time. The results, plotted in Figure 2, show the sensitivity of the analysis to these variables and give an idea of the accuracy that may be expected with ordinary care. Curve C is the standard method given in detail above. The discussion of these curves touches the following points:

1. Concentration of caustic soda solution:

Curves A and F were made with 35.5 sodium hydroxide and 25 per cent sodium hydroxide, respectively, and show less sensitivity for 35.5 per cent soda as regards isopropyl content. Curve F shows complete miscibility with alcohols below 5 per cent in isopropyl content. By comparing C and D made with 30 and 27.5 per cent caustic soda, respectively, it is found that a difference of 1 per cent in the strength of the caustic soda solution used is capable of introducing an error of about 1 per cent in the amount of isopropyl alcohol determined.

2. Temperature of contact:

Curves B and E were made by working at 20° and 40° C., respectively. By comparison with curve C, it is found that a deviation of 1° C. in temperature is capable of introducing an error of about 0.5 per cent in the amount of isopropyl alcohol determined.

3. Proportion of caustic soda solution to alcohol:

Two volumes of caustic soda to one of alcohol were used in the work shown in the graphs. Since the ethyl alcohol and the isopropyl alcohol used contained different amounts of water, it follows that different blends of these alcohols contained varying amounts of water which, in each case, had to come to equilibrium with the caustic soda solution. The large excess of caustic soda avoided any appreciable change in caustic soda strength because of the transfer of varying quantities of water from one phase to the other. A ratio of 4 to 1 was tried instead of 2 to 1. The results were substantially the same.

The effect of changing the caustic soda solution ratio can be seen in the following data, which show the titration obtained when testing various alcohol mixtures by the method described.

2:1 RATIO	4:1 RATIO
39.5	39.1
36.5	36.5
32.4	32.5
28.1	28.1

The divergence is practically within the range of experimental error. From this it is inferred that the amount of caustic soda used need not be measured very accurately.

4. Water content of alcohol:

With alcohol mixtures containing 10 per cent of water or less, the analytical method appears to be accurate. Large concen-

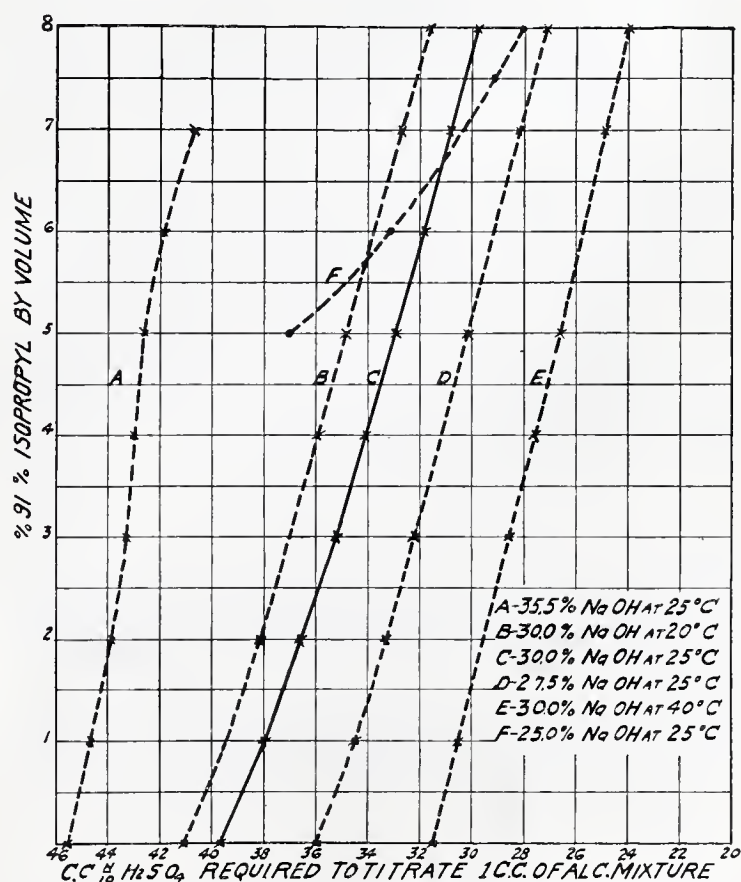


FIGURE 2. ALKALINITY OF ALCOHOL MIXTURES WHEN SHAKEN WITH CAUSTIC SODA

trations of water in the alcohol dilute the caustic soda solution and introduce serious error. Dehydrating such alcoholic mixtures does not offer serious difficulty because the two alcohols are very similar in physical and chemical properties. Dehydration with quicklime was found to be easy and effective. For example, a mixture of 93 per cent of ethyl alcohol and 7 per cent isopropyl alcohol (technical purity in both cases) was diluted 1 to 1 with water and distilled through a bead-packed glass

column, collecting the first 50 per cent cut. This cut was shaken with an excess portion of quicklime and placed in an Engler flask. A small portion was distilled off and collected for analysis. It was found to contain a quantity of alcohol which, calculated on a basis of the original undiluted sample, showed an allowable error of 0.25 per cent isopropyl alcohol.

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Determination of Small Amounts of Ethyl and Butyl Alcohols

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MANY methods have been devised for the determination of ethyl and butyl alcohols in mixtures. Among the recent ones those of Bogin (1) and of Donker (2) make use of the relative insolubility of butyl alcohol in water. The methods of Werkman and Osburn (5) and of Van der Lek (4) involve the oxidation of the alcohols to acids, which are then determined by a suitable method. In the course of an investigation reported elsewhere, it became necessary to determine ethyl and butyl alcohols in small samples of bacterial culture. Since a large number of determinations were to be made, a rapid method was desired. No method making use of solubility differences could be considered because of the large amount of sample required, and methods involving oxidation of the alcohols, steam distillation of the resulting acids, and determination of acetic and butyric acids in the distillate are likely to be slow and cumbersome. It was thought that a method might be devised whereby the acids could be distilled directly from the oxidizing solution in a modified Duclaux procedure. Such a procedure, if feasible, would eliminate the steam distillation and greatly shorten the time necessary for the determination.

After more than a hundred trials in which the effect of a number of variables was studied, a satisfactory procedure was developed. The method to be described has been in use for more than a year, during which time approximately 150 routine determinations have been made. It has been used in a study of the acetone-butyl alcohol organism (3) and has given satisfactory fermentation balances.

EXPERIMENTAL PROCEDURE

REAGENTS. The following reagents were used in this method:

1. Oxidizing solution. Mix equal volumes of exactly 3 *N* potassium dichromate solution and exactly 10 *N* sulfuric acid. Carbon dioxide-free water should be used in making these solutions.

2. Barium hydroxide. Solution 0.1 *N* or 0.02 *N* strength.

3. Indicator solution. To 0.1 gram of phenol red (phenol sulfonphthalein) add 2.85 cc. of 0.1 *N* sodium hydroxide and make up to 500 cc.

APPARATUS. The pieces of apparatus employed were as follows:

1. *Alcohol-distillation apparatus.* The distilling vessel is a Pyrex test tube, 38 by 200 mm. It is connected to a small

A RAPID method for the determination of small amounts (3 to 15 mg.) of ethyl or butyl alcohol or mixtures of the two is described. It is particularly useful in the analysis of bacterial cultures where only small samples are available. The alcohols are oxidized by means of an acid dichromate solution, and the acids produced are distilled directly from the oxidizing solution according to a procedure which makes use of the Duclaux principle. The whole determination may be completed in 40 minutes.

condenser. The lower end of the condenser tube is connected by a short piece of rubber tubing to a glass tube which extends to the bottom of the receiver flask, of 10 cc. capacity, and recalibrated to deliver 10 cc.

2. *Acid-distillation apparatus.* A drawing of this apparatus is given in Figure 1. The distilling vessel, *A*, is a Pyrex test tube, 20 by 200 mm. The condenser tube is made from 8-mm. tubing. The bend at *B* is made as close above the rubber stopper as practicable (1 cm.). The end of the condenser tube, *C*, is drawn out to a tip to facilitate collection of the distillate continuously rather than drop by drop. The receiver is a 10-cc. volumetric flask. Two of these are needed. The flame of the micro-burner heating the test tube is kept constant at any desired size by means of the bubbling bottle *D* and the manometer *F*. The tubes entering the bottle should be of ample size (7 mm.). The excess gas escaping from the bottle is burned. The jet should not be constricted. The size of the flame of the burner may be varied by adjusting cock *E* or by changing the head of water in the bubbling bottle. The burner should be so adjusted that the rate of distillation is fairly rapid, but not so rapid as to permit any mechanical carrying over of liquid. This rate is such that 10 cc. of distillate are collected in 7 or 8 minutes. Once the apparatus is adjusted, the reading on the manometer *F*, and consequently the rate of distillation, should be kept constant. The manometer is filled with paraffin oil or some other non-volatile liquid. A cylindrical shield, *G*, protects the flame from air currents.

3. *Buret.* This should be graduated at 0.01-cc. or at 0.05-cc. intervals, depending upon the strength of alkali used.

A sample of culture containing not more than 15 mg. of total alcohols is placed in the distilling tube of the alcohol-distillation apparatus, made slightly alkaline, and diluted to approximately 20 cc. A few glass beads are added, and the sample is distilled into the 10-cc. receiver flask. About 1 cc. of carbon dioxide-free water is first placed in the flask so that the end of the condenser tube is below the surface throughout the distillation. The distillation should be carried out at a constant rate to prevent sucking back of distillate. The last part of the distillate is collected with the end of the condenser tube above the surface of the distillate. The distillation is continued until the receiver flask is full to the mark. While this distillation is in progress, exactly 10 cc. of oxidizing solution are pipetted into the distilling tube of the acid-distillation apparatus. Four small glass beads are added, and the 10 cc. of alcohol distillate are rinsed into the tube with 5 cc. of carbon dioxide-free water. The tube, which should now contain exactly 25 cc. of reaction mixture, is closed with a rubber stopper and the stopper wired down. The tube is heated in a boiling water bath for exactly 5 minutes, and is

then cooled under the tap, opened, and connected to the acid-distillation apparatus. Two 10-cc. fractions of distillate are collected. This distillation should always be made at the same constant rate. Each fraction is rinsed into a 25-cc. Erlenmeyer flask with carbon dioxide-free water, and titrated with barium hydroxide. A 0.1 *N* barium hydroxide solution is used if the buret is graduated at 0.01-cc. intervals, and a 0.02 *N* solution if the graduations are spaced 0.05 cc. apart. Phenol red is used as indicator, and the end point is taken at a permanent pink color (pH 8.0 to 8.2). A blank determination is run on the reagents alone, and in all cases the titrations obtained are corrected for this blank. The correction should be about 0.01 cc. 0.1 *N* for each fraction. A complete determination may be made in 35 or 40 minutes.

STANDARDIZATION AND CALCULATION. The procedure is standardized on pure ethyl and butyl alcohols. Since the largest source of error in the method is the variability of recovery in the alcohol distillation process, it is best to obtain the constants of the apparatus for ethyl and butyl alcohols without going through the alcohol-distillation step. The recovery of alcohols by distillation may be determined subsequently.

TABLE I. TITRATION CONSTANTS OF ETHYL AND BUTYL ALCOHOL

SAMPLE Mg.	OBSERVED TITRATION (CORRECTED FOR BLANK)		TITRATION PER MG. OF SAMPLE	
	1st fraction Cc. 0.1 <i>N</i>	2nd fraction Cc. 0.1 <i>N</i>	1st fraction Cc. 0.1 <i>N</i>	2nd fraction Cc. 0.1 <i>N</i>
ETHYL ALCOHOL				
15	1.138	1.522	0.0759	0.1014
10	0.759	1.011	0.0759	0.1011
5	0.378	0.508	0.0756	0.1016
2	0.153	0.200	0.0765	0.1000
BUTYL ALCOHOL				
15	1.486	0.497	0.0990	0.0331
10	0.981	0.333	0.0981	0.0333
5	0.490	0.167	0.0980	0.0334
2	0.196	0.069	0.0980	0.0345
ACETONE				
75	0.172	0.192	0.0023	0.0026
25	0.057	0.066	0.0023	0.0026

If 15 cc. of carbon dioxide-free water, containing a known quantity of a single alcohol, are added to 10 cc. of oxidizing solution and the mixture heated and distilled, it will be found that the ratio of the titration values of the two distillate fractions is constant for each alcohol, and that the titration values are directly proportional to the quantity of alcohol present in the sample. If a sample containing both alcohols is oxidized, it will be found that each alcohol behaves, on oxidation and distillation, as if the other were not present. In Table I are given titrations obtained by oxidizing and distilling various quantities of ethyl and butyl alcohols. From the data of Table I the following relationships may be obtained:

$$a = 0.0758E + 0.098B$$

$$b = 0.1011E + 0.0333B$$

where *a* and *b* are the titration values of the first and second fractions, respectively, expressed as cubic centimeters of 0.1 *N* base and *E* and *B* are the quantities of ethyl and butyl alcohols, expressed in milligrams, present in the sample. If we solve the above equations for *B* and *E*, we obtain

$$B = \frac{1.334a - b}{0.0975}$$

$$E = \frac{a - 0.098B}{0.0758}$$

From these formulas, the amount of each alcohol present in an unknown sample may be calculated. Since cultures producing ethyl and butyl alcohols usually produce acetone also, and since acetone is oxidized to a small degree by the dichromate mixture, it is necessary to apply to the titration values a correction proportional to the amount of acetone present.

The acetone is determined independently. In determining the acetone correction, it is essential to use pure acetone. The acetone on the market usually contains about 0.5 per cent of ethyl alcohol.

The calculation of the quantity of each alcohol in a sample is illustrated by the following example:

A sample containing 5 mg. of butyl alcohol, 2 mg. of ethyl alcohol, and 5 mg. of acetone was subjected to oxidation and distillation.

FRACTION	TITRATION		
	Actual Cc. 0.1 <i>N</i>	Corrected for blank Cc. 0.1 <i>N</i>	Corrected for 5 mg. acetone Cc. 0.1 <i>N</i>
<i>a</i>	0.660	0.650	0.639
<i>b</i>	0.390	0.380	0.367

$$B = \frac{(1.334 \times 0.639) - 0.367}{0.0975} = 4.99$$

$$E = \frac{0.639 - (0.098 \times 4.99)}{0.0758} = 1.98$$

Obtained:

4.99 mg. of butyl alcohol
1.98 mg. of ethyl alcohol

When the sample is subjected to the preliminary alcohol distillation, however, the recovery of such small quantities of alcohol is not complete. It has been found by experiment that 2 per cent of the ethyl alcohol and 6 per cent of the butyl alcohol present are lost in this preliminary distillation. The results calculated from the fractional distillation must therefore be divided by 0.98 and 0.94 to give the correct figures for ethyl alcohol and butyl alcohol, respectively.

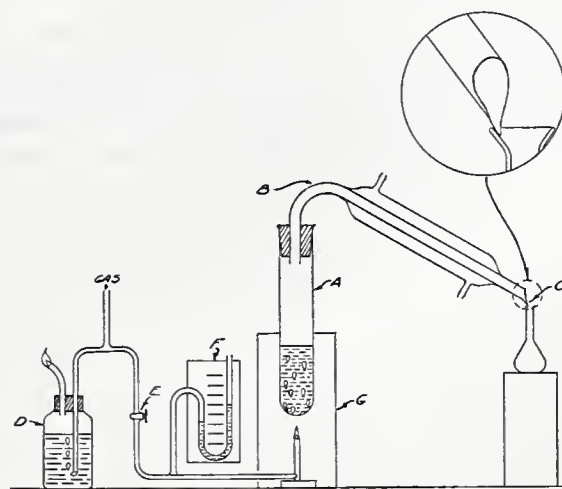


FIGURE 1. ACID-DISTILLATION APPARATUS

ANALYSIS OF KNOWN MIXTURES. In Table II are given the results obtained in a series of determinations where known amounts of acetone, ethyl alcohol, and butyl alcohol were added to 1 per cent peptone solution, and then determined according to the procedure outlined. In the calculations it was assumed that the losses of ethyl and butyl alcohols in the preliminary distillation were those given above. The recoveries are typical of those obtained in a large number of determinations and show that the method is accurate to within 0.1 mg.

TABLE II. RECOVERY OF ALCOHOLS FROM PEPTONE SOLUTION IN PRESENCE OF ACETONE

SAMPLE			FOUND	
Ethyl alcohol Mg.	Butyl alcohol Mg.	Acetone Mg.	Ethyl alcohol Mg.	Butyl alcohol Mg.
10	1	5	9.94	1.04
2	10	5	2.03	10.07
5	5	5	5.02	4.97
1	1	5	1.02	1.00

FACTORS INFLUENCING DETERMINATION

The method just described was adopted after a large number of experiments in which the size of sample, volume of distillate fractions, oxidation time, dichromate concentration, and distillation time were varied. The effect of some of these factors will be discussed in detail.

RATE OF DISTILLATION. In Table III the effect of rate of distillation upon the ethyl alcohol constants is shown. When the rate of distillation is slow, there is more condensation in the upper part of the distilling tube, and the resulting fractionation causes a change in the distilling constants. It is evident, then, that the rate of distillation should be held at some constant value.

TABLE III. EFFECT OF DISTILLATION TIME ON TITRATION CONSTANTS

(Each sample contained 10 mg. of ethyl alcohol)		
TIME OF DISTILLATION Min. Sec.	TITRATION	
	1st fraction Cc. 0.1 N	2nd fraction Cc. 0.1 N
7 4	0.762	1.011
7 55	0.759	1.011
9 0	0.745	1.005
9 48	0.743	1.005

TIME OF OXIDATION. Five minutes of heating are necessary to oxidize the ethyl alcohol. The butyl alcohol is completely oxidized to butyric acid in the first minute or two, and in the course of five minutes a portion of this is further oxidized to acetic acid. That a constant proportion is thus oxidized is shown by the data of Table I, where the ratio of the first titration to the second is constant. The time of oxidation should be held constant so that an unvarying proportion of the butyric acid is oxidized to acetic.

CONCENTRATION OF OXIDIZING SOLUTION AND SIZE OF SAMPLE. It will be noticed that the amount of dichromate added is greatly in excess of the amount required to oxidize the alcohol present. This large amount of dichromate is necessary in order that the initial and final dichromate concentrations may be nearly the same. If the dichromate concentration is low, the change in concentration is sufficient to affect the oxidation of butyric acid to acetic acid materially, and thus to give a "titration constant" for butyl alcohol which is not independent of the size of sample. Even with the dichromate concentration given, if the quantity of alcohol in the sample is too great, the amount of dichromate destroyed is large enough to change its concentration sufficiently to cause a change in the titration constant. A tendency in this direction may be seen in Table I. Fifteen milligrams of butyl alcohol are enough to change the first distillation constant from 0.0980 to 0.0990. If 15 mg. of butyl alcohol are present in a sample, the change in the titration constant is sufficient to reduce the apparent ethyl alcohol content of the sample by 0.14 mg. In some cases, this error would be important. For this reason the sample should never contain more than approximately 15 mg. of alcohols.

CHOICE OF INDICATOR. The titration of the distillate fractions is made somewhat difficult because of the carbon dioxide produced in the oxidation of butyric acid. In dilute solution, carbon dioxide is completely neutralized at a pH of approximately 8.2. When a fading end point, such as is given by carbon dioxide, is encountered in a titration, a two-color indicator is for most observers easier to use than a one-color indicator. Phenol red acquires a red color at pH 8.0, so that it is a satisfactory indicator from the standpoint of pH range. Phenolphthalein, *o*-cresolphthalein, thymol blue, and phenol red have all been used as indicators, but phenol red seems to give the most reliable and most easily reproducible results. The quantity of indicator solution added should, of course, be kept constant.

USE OF METHOD AS QUALITATIVE TEST

This method should not, of course, be used for quantitative measurement of the alcohols present in a culture unless it is known that no alcohols other than ethyl and butyl are present.

In a culture whose alcoholic constituents are unknown, the method may or may not be a valuable qualitative tool. If a determination is run on an unknown culture, and the calculation from the observed titrations indicates the presence of a quantity of ethyl alcohol and of no butyl alcohol, the data may be taken as qualitative and quantitative evidence of the presence of ethyl alcohol in the culture, since it is extremely unlikely that two other alcohols, such as methyl and butyl, are present in the exact proportion to produce the same titration ratio as ethyl alcohol. If, on the other hand, a determination on an unknown sample yields a result indicating the presence of both ethyl and butyl alcohols, it does not follow that these two alcohols are the ones actually present. In general, the method has the same defects, when used qualitatively, as the Duclaux method for acids. While the method as described is intended for use in determining ethyl and butyl alcohols, it may be modified for use in the determination of other pairs of alcohols.

SOURCES OF ERROR AND POINTS OF TECHNIC

Any substance which is readily volatile under alkaline conditions and which will yield carbon dioxide or a volatile acid on oxidation with acid dichromate will interfere with the determination; for instance, several amines and to some extent acetyl methyl carbinol.

The constants given in this paper hold only for the apparatus for which they were determined. If a new apparatus is constructed, the constants must be redetermined. Time will be saved if the volumetric flasks used to collect the acid distillate are calibrated with the inside surface wet. They need not hold precisely 10 cc. provided the flasks used in a determination are the same as were used in standardizing the apparatus. All glassware, including the inner surface of the condenser tube of the acid-distillation apparatus, should be kept scrupulously clean, since, when small volumes of liquid are handled, droplets adhering to glassware introduce a very appreciable error.

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Correction

IN THE PAPER entitled "Determination of Organic Halogen by Liquid Ammonia-Sodium Process" [*IND. ENG. CHEM., Anal. Ed.*, **3**, 274 (1931)], the first word of the fourth line under "Modified Procedure" is "monobutylamine." This should be tributylamine. Inasmuch as monobutylamine forms a salt under the conditions of the procedure, this error is rather serious should anyone attempt to use the method as described.

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October 15, 1931

Colorimetric Determination of Methanol

Interference of Dimethyl Ether

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IN THEIR work on the methanol equilibrium, Smith and Branting (4) made use of a colorimetric method to determine small amounts of methanol. Briefly, the method consisted in oxidizing the methanol to formaldehyde by means of permanganate and then developing the characteristic color with a modified Schiff's reagent. The color of the unknown solution was matched in a colorimeter against that given by standard methanol solutions. Smith and Branting stated that dimethyl ether did not interfere with the determination. von Wettberg (5), working under the writer's direction, made several qualitative tests which indicated quite definitely that dimethyl ether did react and give a color in the absence of any methanol. He generated the gaseous ether by diluting a 40 per cent sulfuric acid solution of it with water. The gas was passed through several water scrubbers in series to remove methanol and formaldehyde, and finally liquefied. The liquid ether was then boiled off through two U-tubes containing water to dissolve the ether. The water solution from these tubes gave a strong test with Schiff's reagent after oxidation. It had previously been demonstrated by experiment that not a trace of methanol would pass the water-scrubbing system. Finally, von Wettberg sealed off a small amount of liquid ether in a bulb, weighed it, and broke the bulb under a known volume of water in a stoppered bottle, thus producing an ether solution of approximately known concentration. This solution was then subjected to a methanol determination by the colorimetric method and found to be 63 per cent equivalent to methanol per methyl group.

On the basis of these results, von Wettberg and Dodge (6) expressed the opinion that the results of Smith and Branting on the methanol equilibrium were somewhat high, in view of the fact that catalysts containing chromium oxide had been shown to produce considerable dimethyl ether. Finally, to clear up this point a series of quantitative determinations have been made, which appear to prove beyond all doubt that dimethyl ether does interfere with the determination of methanol by this method.

PREPARATION OF DIMETHYL ETHER

Pure dimethyl ether was prepared by dropping water into Eastman's 40 per cent solution of ether in sulfuric acid contained in flask A (Figure 1). The gas evolved was scrubbed in U-tubes B, C, and D, containing glass beads wet with water, to remove any methanol and formaldehyde. It is advisable to use a minimum amount of water for scrubbing, since the ether is quite soluble. The gas was dried over anhydrous copper sulfate in E and anhydrous in F, and then condensed to a liquid in bulb G, which was surrounded by a freezing mixture of "Dry-Ice" and alcohol. The ether was then

THIS PAPER demonstrates that dimethyl ether seriously interferes with the determination of methanol by the colorimetric method in spite of statements to the contrary in the literature. It shows that when known dimethyl ether solutions are analyzed by this method, using the same procedure as is used on unknown methanol solutions, the ether is approximately 67 per cent equivalent to methanol per methyl group, or 1 gram of ether is equivalent to 0.93 gram of methanol.

distilled back and forth between the two bulbs G and J several times, each time rejecting the first and last portions of the liquid and condensing only a middle fraction. Distillates were rejected by allowing the gas to escape to the atmosphere through cock 3. The manometer, H, filled with mercury, was useful in controlling the rate of distillation. After a few redistillations, the middle portion of the condensed liquid was

distilled to a mercury-sealed storage pipet. It was deemed unnecessary to make any tests to determine the purity of the ether because the method of preparation insured its high purity. Nevertheless, the precaution was taken of showing that a water solution of the ether did not produce color with Schiff's reagent. This insures the absence of formaldehyde, the only organic compound with a boiling point near that of the ether which might reasonably be expected to be present in traces. Furthermore, the work of Maas and Russell (3) and of Cardoso (2) shows that pure methyl ether is obtained in this way.

BEHAVIOR OF ETHER TOWARD METHANOL TEST

To study the effect of the ether on the method of analysis used for methanol, it was necessary to prepare dilute, known

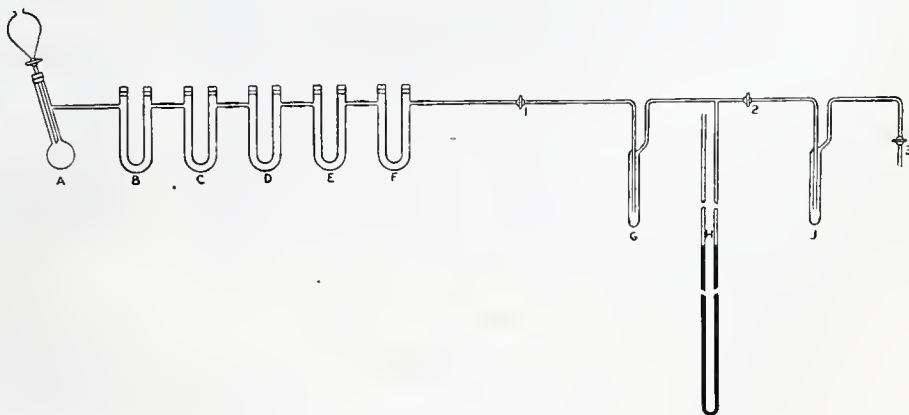


FIGURE 1. APPARATUS FOR PREPARING DIMETHYL ETHER

solutions of methyl ether in water. Several methods of doing this were tried before a reasonably simple and satisfactory way was evolved. About 60 to 80 cc. of the gaseous ether from the mercury-sealed pipet were drawn into the mercury-sealed buret B of Figure 2 and measured at the pressure of the atmosphere. Approximately 100 cc. of water were placed over the mercury in another pipet, C, leaving no gas space over the water. Some of the methyl ether from the buret was passed through a previously flushed-out capillary tube into C. After most of the gas had dissolved, the small residue was drawn back to the buret and the volume in the buret again measured to give by difference the volume of ether dissolved. The ether solution was then passed into a 250-cc. volumetric flask and made up to 250 cc. with water, some of which had been used to rinse out the pipet. Very

little, if any, ether would be lost in this transfer, because it is fairly soluble in water and the solution was very dilute.

A number of standard solutions of methanol in water were made up by mixing weighed amounts of pure methanol with a liter of water. The concentration of the standards varied from 1 part of methanol to 1500 parts of water, to 1 in 7500 in steps of 500 parts of water. It was later found that concentrations in the neighborhood of 1 part in 2000 gave about the most satisfactory depth of color for comparison, and these were used exclusively in the work to be reported.

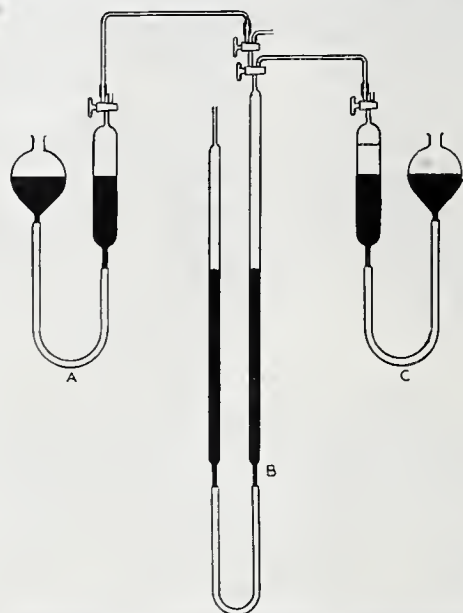


FIGURE 2. APPARATUS FOR PREPARING DIMETHYL ETHER SOLUTIONS

A direct comparison between a standard methanol solution and the methyl ether solution was obtained by taking 10 cc. of each with a pipet and treating them practically simultaneously by the same procedure. The oxidation by permanganate and subsequent reduction of excess potassium permanganate was done according to the procedure of Wright (7). The Schiff's reagent was made up according to Alyea and Bäckström (1). The apparent methanol concentration of the ether solution was obtained by multiplying the concentration of the standard by the ratio of the depth readings on the two sides of the colorimeter. Conditions were so chosen that the color concentration in the standard was not very different from that in the ether solution. Comparisons were made with a Duboscq biological colorimeter (Bausch and Lomb No. 2400 D).

The experimental data are summarized in Tables I and II.

TABLE I. DATA ON ETHER SOLUTIONS

SOLN. No.	ETHER Cc.	PRESSURE Mm. Hg	TEMPERATURE ° C.	CONCENTRATION OF SOLN.
				Gram/liter
1	41.17	766.3	26.0	0.312
2	40.35	761.0	23.2	0.307
3	56.50	765.0	25.5	0.429
4	56.40	765.0	25.5	0.428

TABLE II. RESULTS OF COLORIMETER COMPARISONS

COMPARISON No.	SOLN. No.	EQUIVALENT MeOH %
1	1	71.8
2	1	72.9
3	1	61.5
4	2	72.3
5	3	68.8
6	4	72.1
7	1	73.0
8	2	67.5
9	3	64.8
10	4	65.2
11	1	63.5
12	2	62.8
13	3	60.1
14	4	61.7
	Av.	67.0

Fourteen colorimeter comparisons were made using the four ether solutions given in Table I. The results of these comparisons, expressed as equivalent per cent methanol, are given in Table II.

Comparisons 3 to 10, inclusive, were made with a new set of reagents and standards, as compared with numbers 1 and 2. Comparisons 11 to 14 were made on the identical solutions used in tests 7 and 10, but with an additional time of standing.

Equivalent per cent methanol is obtained from the colorimeter comparisons as follows: When solution 3 is compared with a methanol standard containing 0.500 gram per liter and the depth readings are 30.0 and 36.6, respectively, for the standard and the ether solution, the apparent methanol concentration of the ether solution is:

$$\frac{300}{366} \times 0.500 = 0.410 \text{ gram per liter}$$

The equivalent methanol concentrations of the ether solution on the basis of equivalence of methyl groups is

$$0.429 \times \frac{64}{46} = 0.595 \text{ gram per liter}$$

Hence, equivalent per cent methanol

$$\frac{0.410}{0.595} \times 100 = 68.8\%$$

The results are not very closely reproducible. This is believed to be largely due to the fact that the oxidation reaction is not clean cut and definite and the amount of aldehyde present in the solution is dependent on a considerable number of factors, many of which are difficult to control. To study these factors with a view to obtaining more exact results is beyond the scope of this work and hardly seems worth while. It should be noted that much more closely reproducible results have been obtained when pure methanol solutions are analyzed by this method. In such a case, checks within 1 per cent are readily obtained after experience has been gained. When impurities are present in methanol, the reproducibility becomes less, even though the impurities do not directly interfere.

The average equivalent per cent methanol from these fourteen comparisons checks fairly well with the earlier figure (63 per cent) obtained by von Wettberg using an entirely different set of reagents and standards and a wholly different method of preparing the ether solutions.

ACKNOWLEDGMENT

The experimental work on which this paper is based was carried out at various times by E. F. von Wettberg, Jr., E. B. Wilson, and F. J. Sanders, while graduate students at Yale.

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RECEIVED August 1, 1931.

NEW DETERGENT. Research has been in progress for some time in the I. G. laboratories to develop soap-like products of improved properties. Recognizing that normal soaps have limitations, especially with regard to solubility, behavior in hard water, and detergent power, the first of the new series for industrial and household use is said to overcome these faults.

Citrate-Insoluble Phosphoric Acid in Di- and Tricalcium Phosphates

Some Factors Affecting Its Determination

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WHEN ordinary superphosphate is treated with ammonia, a portion of the original water-soluble phosphoric acid (P_2O_5) is converted into water-insoluble forms. Addition of more than about 2 per cent of ammonia results in the formation of phosphates which are also insoluble in neutral ammonium citrate solution as determined by the official method (1), the quantity of citrate-insoluble phosphoric acid increasing with the quantity of ammonia added. Recent investigations (13, 15) indicate that the citrate-soluble and the citrate-insoluble phosphates formed under these conditions consist principally of dicalcium and tricalcium phosphates, respectively. In view of the fact that heavily ammoniated superphosphate¹ contains a relatively large portion of its phosphoric acid in the form of di- and tricalcium phosphates, information on the factors affecting the solubilities² of these two compounds in ammonium citrate solutions is of particular importance.

Fresenius, Neubauer, and Luck (7) first proposed, in 1871, the use of ammonium citrate solutions for the laboratory determination of the so-called "available" phosphoric acid in water-insoluble phosphates. Since that time, numerous experiments have been carried out on the solubilities of di- and tricalcium phosphates in citrate solutions. The reported results, particularly those of the earlier investigators (5, 6, 8, 9, 11, 16), are, however, very conflicting. As pointed out by Robinson (19) in his excellent review of the work on the subject published prior to 1919, this is no doubt owing largely to the variable and uncertain pH values of the citrate solutions used by the different investigators. The discrepancies are also probably due in part to the fact that in many cases the experiments were made with mixtures of phosphates rather than with the individual compounds. Furthermore, no single comprehensive investigation of the factors affecting the citrate solubilities of these phosphates under definitely known and reproducible conditions seems to have been made.

The present paper gives the results of a study of the citrate solubility of tricalcium phosphate as affected by the weight of sample, the time of digestion with citrate solution, the size of the phosphate particles, the pH and specific gravity of the citrate solution, the presence of other compounds, and by heating the phosphate prior to the citrate digestion. The effect of several of these factors on the solubility of dicalcium phosphate was also determined.

THE WATER-INSOLUBLE di- and tricalcium phosphates are becoming of increasing importance in the fertilizer industry because of their occurrence in ammoniated superphosphates. Investigations with the pure salts show that the solubilities of these compounds in ammonium citrate solution are affected to a considerable extent by the weight of sample taken for analysis, the presence of other salts, the pH of the citrate solution, and the temperature at which the salt is heated before the citrate digestion. The solubilities are affected to a less extent by the fineness of the particles, the gravity of the citrate solution, and the time of the citrate digestion.

PHOSPHATE MATERIALS USED

DICALCIUM PHOSPHATE. Sample 387 was Baker and Adamson's c. p. material. It appeared to be in the amorphous condition and the analysis indicates that it was the anhydrous salt. Sample 390 was Kahlbaum's c. p. crystalline material containing approximately 2 moles of water of crystallization. The phosphoric acid-lime ratios indicate that both materials contained slightly more lime than is theoretically required for the pure salt.

TRICALCIUM PHOSPHATE. Samples 287, 1023, and 1093 were sold as c. p. materials by Eimer and Amend, Baker and Adamson, and Merck, respectively. The phosphoric acid-lime ratios indicate that these materials contained more lime than is theoretically required for the pure salt. Sample 1094 was prepared by neutralizing a water suspension of pure calcium hydroxide with a dilute solution of pure phosphoric acid, evaporating to dryness on the steam bath, and finally heating at 900° to 950° C., as described by Jacob and Reynolds (14). Sample 1095 was prepared by slowly adding a solution of pure trisodium phosphate to a solution containing a small excess of calcium nitrate. The precipitate was washed with a saturated solution of tricalcium phosphate until the filtrate gave no test for nitrates, the salt finally being dried at a temperature of 50° C.

The composition of the samples is given in Table I.

TABLE I. COMPOSITION OF PHOSPHATES

SAM- PLE	P ₂ O ₅ %	ALKALIES CaO %	R ₂ O %	Cl %	NITRATE N %	IGNITION LOSS AT 1100° C. %	P ₂ O ₅ - CaO RATIO
DICALCIUM PHOSPHATE ^a							
387	50.45	40.25	26.35 ^b	1.253
390	42.29	34.02		1.243
TRICALCIUM PHOSPHATE ^c							
287	40.86	49.50	2.70	0.00	0.005	6.74	0.825
1023	40.44	50.25	1.55	0.40	0.002	6.70	0.805
1093	41.82	51.22	0.88	0.00	0.009	5.44	0.816
1094	45.38	54.36	0.00	0.00	0.000	0.27	0.835
1095	40.48	47.46	0.56	0.00	0.103	10.97	0.853

^a Theoretical P_2O_5 -CaO ratio = 1.267.
^b Loss at 900° C.
^c Theoretical P_2O_5 -CaO ratio = 0.845.

METHOD OF DETERMINING CITRATE-INSOLUBLE PHOSPHORIC ACID

When tricalcium phosphate is treated with citrate solution according to the official method, clear filtrates are difficult to obtain because a portion of the phosphate usually passes through the filter paper in the colloidal condition, and results in low values for citrate-insoluble phosphoric acid. Clear filtrates may be obtained, however, by the use of short Pas-

¹ The term ammoniated superphosphate refers to ordinary superphosphate that has been treated with anhydrous or aqueous ammonia.
² The term "solubility" as used in this paper refers to solubility as determined under certain specified conditions which are not necessarily equilibrium conditions.

teur-Chamberland filter tubes. Duplicate results thus obtained are usually in good agreement and, in the case of phosphates which filter clear through paper, check closely those obtained by the use of filter paper. These tubes were used in obtaining all the results for citrate-insoluble phosphoric acid given in the present paper.

Except for the method of filtration and as noted otherwise, the official procedure was carefully followed on 100-mesh material. The neutral citrate solution was carefully prepared according to the official method (1), using phenol red as an indicator. This solution had a true pH value of 6.95 at 20° C. as determined potentiometrically by means of the hydrogen electrode. In all cases 100 cc. of the citrate solution were used.

proportional to the weight of sample when 0.5- to 2.0-gram samples were used. On the other hand, the weights of phosphoric acid dissolved from 2.0-gram samples of tricalcium phosphate were only 1.2 to 1.7 times those dissolved from 0.5-gram samples, indicating that as the weight of sample was increased the amount of phosphoric acid dissolved by the citrate solution rapidly approached the maximum amount that could be dissolved under the conditions of the determinations.

The investigations of Zulkowski and Cedivoda (23) indicate that the dissolution of calcium phosphates by citrate solution is due to reactions which result in the formation of ammonium phosphates and calcium citrates, or calcium ammonium citrates. As shown by the figures in Table III,

TABLE II. EFFECT OF WEIGHT OF SAMPLE ON CITRATE SOLUBILITY OF DI- AND TRICALCIUM PHOSPHATES

(Samples digested for 30 minutes at 65° C.)

SAMPLE	CITRATE-INSOLUBLE P_2O_5 AS PERCENTAGE OF:								P_2O_5 DISSOLVED BY 100 CC. OF CITRATE SOLN.				P_2O_5 DISSOLVED BY 100 CC. OF CITRATE SOLN. ON BASIS OF UNITY FOR 0.5-GRAM SAMPLES			
	Sample				Total P_2O_5				Wt. of sample:				Wt. of sample:			
	0.5 g. %	1.0 g. %	1.5 g. %	2.0 g. %	0.5 g. %	1.0 g. %	1.5 g. %	2.0 g. %	0.5 g. Mg.	1.0 g. Mg.	1.5 g. Mg.	2.0 g. Mg.	0.5 g. %	1.0 g. %	1.5 g. %	2.0 g. %
DICALCIUM PHOSPHATE																
387	0.00	0.00	2.48	8.12	0.0	0.0	4.9	16.1	252.3	504.5	719.6	846.6	1.00	2.00	2.85	3.36
390	0.00	0.00	0.36	2.33	0.0	0.0	0.9	5.5	211.5	422.9	629.0	799.2	1.00	2.00	2.97	3.78
TRICALCIUM PHOSPHATE																
287	14.54	23.60	28.40	31.17	35.6	57.8	69.5	76.3	131.6	172.6	186.9	193.8	1.00	1.31	1.42	1.47
1023	7.67	20.46	26.82	28.61	19.0	50.6	66.3	70.7	163.9	199.8	204.3	236.6	1.00	1.22	1.25	1.44
1093	14.06	24.99	29.36	32.05	33.6	59.8	70.2	76.6	138.8	168.3	186.9	195.4	1.00	1.21	1.35	1.41
1094	10.24	24.43	30.96	34.65	22.6	53.8	68.2	76.4	175.7	209.5	216.3	214.6	1.00	1.19	1.23	1.22
1095	7.14	19.48	23.30	26.38	17.6	48.1	57.6	65.2	166.7	210.0	257.7	282.0	1.00	1.26	1.55	1.69

EFFECT OF WEIGHT OF SAMPLE

The figures given in Table II show that the dicalcium phosphates were completely soluble in citrate solution when the weight of sample did not exceed 1.0 gram, but with larger samples a portion of the phosphoric acid was insoluble under the conditions of the experiments, the quantity increasing with the weight of sample. Although higher percentages of citrate-insoluble phosphoric acid were obtained from the 1.5- and 2.0-gram samples of the anhydrous dicalcium phosphate, sample 387, than from the hydrated material, sample 390, under corresponding conditions, it will be noted that the anhydrous material originally contained a much higher percentage of total phosphoric acid, and that larger actual weights of phosphoric acid were dissolved from it. Haskins (10) has shown that the percentage of citrate-insoluble phosphoric acid in commercial "precipitated" phosphate, obtained as a by-product of the manufacture of glue and gelatin from bones, is decreased to a considerable extent by reducing the weight of the sample from 2.0 grams to 1.0 gram. Although this type of precipitated phosphate consists essentially of dicalcium phosphate, Haskin's failure to obtain complete solution of the phosphoric acid in 1.0-gram samples indicates that his materials may have contained some tricalcium phosphate.

In the case of tricalcium phosphate, there was a progressive and significant decrease in the percentage of citrate-insoluble phosphoric acid when the weight of sample was decreased by 0.5-gram steps from 2.0 grams to 0.5 gram, the change being greater when the weight of sample was decreased from 1.0 gram to 0.5 gram than from 2.0 grams to 1.0 gram. The results show that the citrate solubility of tricalcium phosphate varies somewhat with different samples, and that approximately 65 to 75 per cent of the total phosphoric acid is insoluble, under the conditions prescribed by the official method, when 2.0-gram samples are used. When the weight of sample is reduced, however, to 0.5 gram, only about 18 to 36 per cent of the total phosphoric acid is insoluble.

In the case of dicalcium phosphate, the weight of phosphoric acid dissolved by 100 cc. of citrate solution was roughly

the dissolution of unignited di- and tricalcium phosphates is also accompanied by reactions that, where complete solution of the phosphates is not obtained, result in the formation of citrate-insoluble residues, which contain a lower ratio of phosphoric acid to lime than is present in the original phosphates. The residues contained less than 0.1 per cent of ammonia nitrogen.

TABLE III. P_2O_5 -CaO RATIOS IN CITRATE-INSOLUBLE RESIDUES FROM DI- AND TRICALCIUM PHOSPHATES

SAMPLE	Original material	P ₂ O ₅ -CaO RATIOS ^a			
		Citrate-Insoluble Residues			
		Wt. of sample:			
		0.5 g.	1.0 g.	1.5 g.	2.0 g.
DICALCIUM PHOSPHATE					
387	1.253	1.127	1.189
390	1.243	0.910
TRICALCIUM PHOSPHATE					
287	0.825	0.760	0.786	0.796	0.792
1023	0.805	0.775	0.757	0.775	0.754
1093	0.816	0.781	0.767	0.763	0.779
1094 ^b	0.835	0.813	0.832	0.839	0.830
1095	0.853	0.752	0.787	0.786	0.783

^a Theoretical ratio for dicalcium phosphate = 1.267; for tricalcium phosphate = 0.845; for calcium hydroxyphosphate = 0.760.

^b Heated at 900° to 950° C.

Many years ago Warrington (22) observed that tricalcium phosphate hydrolyzes in water to give a product containing an excess of lime. Lorah, Tartar, and Wood (17) have recently made a more thorough investigation of this reaction and conclude that a product corresponding in composition to hydroxyapatite, $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$, is finally obtained by the prolonged treatment of tricalcium phosphate with large quantities of boiling water. Buch (4) observed that prolonged treatment of dicalcium phosphate with water also results in the formation of more basic phosphates.

Hydrolysis of the calcium phosphates is a slow process in pure water, but is quite rapid in neutral ammonium citrate solution. The phosphoric acid-lime ratios in the residues from unignited tricalcium phosphate are close to the ratio required for the hydroxyphosphate. Hydrolysis does not seem to occur to a significant extent, however, in the case of some samples of tricalcium phosphate that have been ignited at 900° to 950° C. (sample 1094). The results given in

Table IV show that the citrate solubility of citrate-insoluble residues obtained from tricalcium phosphate is quite different from that of the original phosphate. The residue used in these experiments was obtained by treating 100 grams of tricalcium phosphate, sample 287, with 20 liters of citrate solution, as described in a previous paper (13).

TABLE IV. SOLUBILITY OF RESIDUE FROM CITRATE EXTRACTION OF TRICALCIUM PHOSPHATE 287

	TOTAL P ₂ O ₅	P ₂ O ₅ -CaO RATIO	P ₂ O ₅ DISSOLVED BY 100 CC. OF CITRATE SOLN. Wt. of sample:			
			0.5 g.	1.0 g.	1.5 g.	2.0 g.
			Mg.	Mg.	Mg.	Mg.
Original material	40.86	0.825	131.6	172.6	186.9	193.8
Citrate-insoluble residue	38.68	0.774	59.2	69.9	73.2	86.6

EFFECT OF PH OF CITRATE SOLUTION

Many investigators (19) have shown that the solubility of phosphates in citrate solution depends to a considerable extent on the reaction of the solution, the solubility of the calcium phosphates increasing with the acidity of the solution. This accounts for the discordant results reported by many of the early workers who had no accurate method for determining the true reaction of their solutions. The reaction of citrate solutions can now be accurately determined and controlled, however, by the use of potentiometric and colorimetric methods (19, 20). Robinson (19) found that in the case of tricalcium phosphate, the percentage of total phosphoric acid present as citrate-insoluble phosphoric acid was 74.1, 79.7, 80.3, and 82.8, as determined by the official method using 2-gram samples, when the pH values of the citrate solutions were 6.6, 7.0, 7.4, and 7.8, respectively. Robinson's solutions were all adjusted to a specific gravity of 1.09 at 20° C., and, consequently, 100 cc. of the solutions probably did not contain identical quantities of the citrate radical.

In order to obtain information on the effect of pH on the solubility of tricalcium phosphate when the concentration of citrate radical was maintained constant, several solutions containing exactly 188.13 grams of pure crystallized citric acid, C₆H₈O₇·H₂O, per liter³ at 20° C. were prepared as follows:

Five portions of 188.13 grams each of pure citric acid were weighed into separate liter flasks and dissolved in about 400 cc. of water. The solutions were roughly neutralized to the desired pH values by the addition of strong ammonium hydroxide, care being taken not to overstep the particular pH values desired. The reactions of the solutions were then carefully adjusted colorimetrically to the desired pH values by the addition of small quantities of dilute ammonium hydroxide. Bromothymol blue was used as an indicator in preparing the solutions with pH values of 6.6 and 6.8, while phenol red was used in preparing those with higher values. Ammonium citrate solution neutralized to a pH of 7.0 as determined colorimetrically using bromothymol blue has an actual pH value of about 6.8 as determined potentiometrically using the hydrogen electrode. Consequently, when this indicator was used the solutions were adjusted to apparent pH values 0.2 higher than those actually desired. Values obtained colorimetrically by the use of phenol red are only about 0.05 pH lower than those obtained with the hydrogen electrode. All the test portions were returned to the flasks and the solutions were diluted to 1 liter. The reactions of the solutions were finally determined potentiometrically using the hydrogen electrode.

The figures given in Table V show that, with a constant concentration of citrate radical in the pH range 6.6 to 7.3, a difference of 0.2 pH in the reaction of the solution had an appreciable effect on the solubility of tricalcium phosphate. These results indicate that careful adjustment of the reaction

³ As an average of tests on eight carefully prepared solutions, Robinson (19) found that 1 liter of a citrate solution having a pH of 7.0 and a specific gravity of 1.09 at 20° C. contains 172 grams of anhydrous, or 188.13 grams of crystallized, citric acid monohydrate.

of the citrate solution is very important in determining the solubility of tricalcium phosphate.

TABLE V. EFFECT OF PH OF CITRATE SOLUTION ON SOLUBILITY OF TRICALCIUM PHOSPHATE 287

(Samples digested for 30 minutes at 65° C.)

PH OF CITRATE SOLN. ^a	SP. GR. OF CITRATE SOLN.	CITRATE-INSOLUBLE P ₂ O ₅ AS PERCENTAGE OF:			
		Sample		Total P ₂ O ₅	
		Wt. of sample: 0.5 g.	Wt. of sample: 2.0 g.	Wt. of sample: 0.5 g.	Wt. of sample: 2.0 g.
6.63	1.092	12.61	30.14	30.9	73.8
6.76	1.091	13.81	30.67	33.8	75.1
6.91	1.092	14.45	31.13	35.4	76.2
7.09	1.092	15.88	31.73	38.9	77.7
7.27	1.091	16.62	32.04	40.7	78.4

^a Values determined at 20° C. by means of hydrogen electrode.

EFFECT OF SPECIFIC GRAVITY OF CITRATE SOLUTION

The figures given in Table VI show that the solubility of 1-gram samples of tricalcium phosphate, sample 287, was not affected to a significant extent by small changes in the specific gravity of the citrate solution within the gravity range of 1.090 to 1.094. Reducing the gravity of the solution to 1.088 and 1.086, respectively, resulted, however, in progressive and appreciable increases in the percentages of citrate-insoluble phosphoric acid. The citrate solutions used in these experiments were prepared as follows:

Five liters of solution, neutral to phenol red and having a gravity greater than 1.094, were prepared. This solution was divided into five portions, and the gravities were adjusted to the desired values at 20° C., as determined by the hydrometer.

At gravities of 1.086 to 1.094, addition of about 20 cc. of water per liter changes the gravity of neutral ammonium citrate solution by about 0.002, which corresponds to a change of about 2.0 per cent in the concentration of the solutions. Consequently, in the case of the 1-gram samples of tricalcium phosphate 287, a progressive reduction of 0.002 in the gravity of the citrate solution might be expected to produce a progressive increase of about 0.50 per cent in the amount of citrate-insoluble phosphoric acid. The results given in Tables II and VI show, however, that within the limits of the experiments the solubility of this compound is not a linear function of either the concentration or the total volume of the citrate solution.

TABLE VI. EFFECT OF SPECIFIC GRAVITY OF CITRATE SOLUTION ON SOLUBILITY OF TRICALCIUM PHOSPHATE 287

(1-gram samples digested for 30 minutes at 65° C.)

SP. GR. OF CITRATE SOLN.	CITRATE-INSOLUBLE P ₂ O ₅ AS PERCENTAGE OF:	
	Sample	Total P ₂ O ₅
	%	%
1.086	25.29	61.9
1.088	24.91	61.0
1.090	24.44	59.8
1.092	24.41	59.7
1.094	24.32	59.5

Although the directions for the preparation of the official citrate solution specify that it shall have a specific gravity of 1.09 at 20° C., no statement is given as to the temperature at which the 100-cc. aliquots used for the determination of insoluble phosphoric acid shall be drawn. The temperature of the citrate solution at the time the aliquot is drawn may range from 15° to 35° C. in different laboratories and in the same laboratory at different seasons of the year. Tests on a neutral solution that had a gravity of 1.090+ at 20° C., as determined by the hydrometer, showed that the gravity was 1.092 at 15°, 1.089 at 25°, 1.088 at 30°, and 1.087 at 35° C. A change in gravity is of course accompanied by a change in the total weight of citrate radical in 100 cc. of the solution. Within the range of temperatures usually encountered in the laboratory this change in concentration will probably have no effect on the determination of citrate-insoluble phosphoric acid in such materials as straight superphosphates, double

or triple superphosphates, and the usual types and grades of mixed fertilizers, but it may be of significance in the case of pure tricalcium phosphate, highly ammoniated superphosphate, and bone materials.

EFFECT OF PARTICLE SIZE

A sample of 100 grams of tricalcium phosphate, sample 287, was separated into particle-size ranges of 20 to 50 mesh (0.864 to 0.254 mm.), 50 to 100 mesh (0.254 to 0.147 mm.), finer than 100 mesh, and finer than 200 mesh (0.074 mm.). The different particle sizes had the same content of total phosphoric acid. The figures given in Table VII show that under the conditions of the experiments the solubility of tricalcium phosphate increased as the size of particle was decreased to 100 mesh. Although the figures for citrate-insoluble phosphoric acid are somewhat higher in the 200-mesh material than in the 100-mesh material, the differences are probably of no significance. The effect of particle size became less pronounced as the weight of sample was increased from 0.5 gram to 2.0 grams.

TABLE VII. EFFECT OF PARTICLE SIZE ON CITRATE SOLUBILITY OF TRICALCIUM PHOSPHATE 287

(Samples digested for 30 minutes at 65° C.)

WT. OF Ca ₃ PO ₄ Grams	PARTICLE SIZE Mesh	CITRATE-INSOLUBLE P ₂ O ₅ AS PERCENTAGE OF:	
		Sample	Total P ₂ O ₅
		%	%
0.5	20-50	21.89	53.6
0.5	50-100	18.44	45.1
0.5	< 100	14.54	35.6
0.5	< 200	14.83	36.3
1.0	20-50	27.84	68.1
1.0	50-100	26.55	65.0
1.0	< 100	23.60	57.8
1.0	< 200	24.07	58.9
2.0	20-50	32.39	79.3
2.0	50-100	31.95	78.2
2.0	< 100	31.17	76.3

EFFECT OF TIME OF DIGESTION

The results given in Table VIII show that when 0.5-gram samples were used, the amount of citrate-insoluble phosphoric acid in unignited tricalcium phosphate was decreased to a significant extent by increasing the time of digestion from 0.5 hour to 1.0 hour, but with 1.0- and 2.0-gram samples the effect was much less. In general, increasing the time of digestion from 1.0 hour to 1.5 hours had no significant effect on the amount of citrate-insoluble phosphoric acid. When the tricalcium phosphate was ignited at 1000° C. there was, however, a progressive and significant decrease in the quantity of citrate-insoluble phosphoric acid as the time of digestion was increased from 0.5 hour to 1.5 hours.

TABLE VIII. EFFECT OF TIME OF DIGESTION ON CITRATE SOLUBILITY OF TRICALCIUM PHOSPHATE

(Samples digested at 65° C.)

WT. OF Ca ₃ (PO ₄) ₂ <i>Grams</i>	TIME OF DIGESTION <i>Hours</i>	CITRATE-INSOLUBLE P ₂ O ₅ AS PERCENTAGE OF:		P ₂ O ₅ DISSOLVED BY 100 CC. OF CITRATE SOLN. <i>Mg.</i>
		Sample	Total P ₂ O ₅	
		%	%	
Ca ₃ (PO ₄) ₂ 1095				
0.5	0.5	7.14	17.6	166.7
0.5	1.0	4.69	11.6	179.0
0.5	1.5	4.00	9.9	182.4
1.0	0.5	19.48	48.1	210.0
1.0	1.0	17.81	44.0	226.7
1.0	1.5	18.19	44.9	222.9
Ca ₃ (PO ₄) ₂ 287				
0.5	0.5	14.54	35.6	131.6
0.5	1.0	12.66	31.0	141.0
0.5	1.5	12.58	30.8	141.4
1.0	0.5	23.60	57.8	172.6
1.0	1.0	23.26	56.9	176.0
1.0	1.5	23.15	56.7	177.1
2.0	0.5	31.17	76.3	193.8
2.0	1.0	30.46	74.5	208.0
2.0	1.5	30.26	74.1	212.0
1.0 ^a	0.5	26.17	64.0	146.9
1.0 ^a	1.0	24.99	61.2	158.7
1.0 ^a	1.5	23.94	58.6	169.2

^a Ignited for 1 hour at 1000° C. prior to citrate digestion.

TABLE IX. EFFECT OF CALCIUM SULFATE AND CALCIUM CARBONATE ON CITRATE SOLUBILITY OF DICALCIUM PHOSPHATE 390

(Samples digested for 30 minutes at 65° C.)

WT. OF CaHPO ₄ · 2H ₂ O Grams	WT. OF ADDED MATERIAL Grams	CITRATE-INSOLUBLE P ₂ O ₅ AS PERCENTAGE OF:		Total P ₂ O ₅	
		Sample Added material:		Added material:	
		CaSO ₄ · 2H ₂ O ^a	CaCO ₃ ^b	CaSO ₄ · 2H ₂ O	CaCO ₃
1.0	0.0	0.00	0.00	0.0	0.0
1.0	0.5	Trace	1.21	..	2.9
1.0	1.0	0.93	2.43	2.2	5.7
1.0	2.0	3.99	3.82	9.4	9.0
2.0	0.0	2.33	2.33	5.5	5.5
2.0	0.5	4.68	5.97	11.1	14.1
2.0	1.0	6.24	7.16	14.8	16.9
2.0	2.0	8.25	8.51	19.5	20.1

^a Synthetic gypsum.

^b Synthetic calcium carbonate.

TABLE X. EFFECT OF CALCIUM SULFATE AND CALCIUM CARBONATE ON CITRATE SOLUBILITY OF TRICALCIUM PHOSPHATE 1095

(Samples digested for 30 minutes at 65° C.)

WT. OF Ca ₃ (PO ₄) ₂ Grams	WT. OF ADDED MATERIAL Grams	CITRATE-INSOLUBLE P ₂ O ₅ AS PERCENTAGE OF:		Total P ₂ O ₅	
		Sample Added material:		Added material:	
		CaSO ₄ ·2H ₂ O ^a	CaCO ₃ ^b	CaSO ₄ ·2H ₂ O	CaCO ₃
0.5	0.0	7.14	7.14	17.6	17.6
0.5	0.5	16.25	25.56	40.1	63.1
0.5	1.0	23.12	30.74	57.1	75.9
0.5	2.0	33.10	34.12	81.8	84.3
1.0	0.0	19.48	19.48	48.1	48.1
1.0	0.5	24.88	30.35	61.5	75.0
1.0	1.0	29.35	33.31	72.5	82.3
1.0	2.0	35.28	35.35	87.2	87.3
2.0	0.0	26.38	26.38	65.2	65.2
2.0	0.5	30.66	33.81	75.7	83.5
2.0	1.0	33.40	35.64	82.5	88.0
2.0	2.0	36.90	37.54	91.2	92.7

^a Synthetic gypsum.

^b Synthetic calcium carbonate.

It is interesting to note that in the case of unignited tricalcium phosphate, sample 287 for instance, the actual weights of phosphoric acid dissolved when 0.5- to 2.0-gram samples were digested for 1.5 hours depended upon the weight of sample, and showed no significant increases over the weights dissolved when the samples were digested for 1 hour. From this it may be concluded that with each particular weight of sample, the citrate solution dissolved during the course of 1 hour approximately the maximum weight of phosphoric acid that it was capable of dissolving under the conditions of the experiments. The question then arises as to why greater weights of phosphoric acid were dissolved when 2-gram samples were digested for 1 hour than when 0.5- or 1-gram samples were digested under the same conditions. At present the reason for this is not entirely clear, but the data given in Tables II, III, and VIII indicate that the action of citrate solutions on tricalcium phosphate involves not only the dissolution of some tricalcium phosphate, but also the hydrolysis of a portion of the tricalcium phosphate to calcium hydroxyphosphate, and the dissolution of a certain amount of the last compound. Calcium hydroxyphosphate is much more insoluble in citrate solution than is tricalcium phosphate, and it may be that a relatively greater proportion of the original tricalcium phosphate is converted into hydroxyphosphate when the weight of sample is decreased from 2.0 grams to 0.5 gram.

EFFECT OF OTHER COMPOUNDS

The results given in Tables IX and X show that gypsum and calcium carbonate had a very pronounced effect in decreasing the citrate solubilities of the di- and tricalcium phosphates. Calcium carbonate had a greater effect than an equal weight of gypsum, and both had a much greater effect on the solubility of tricalcium phosphate than on dicalcium phosphate. Both gypsum and calcium carbonate had a more pronounced effect when 0.5-gram samples of tricalcium phosphate were used than when 1- and 2-gram samples were used. The effect of these compounds on the solubilities of di-

and tricalcium phosphates is of considerable practical importance, since ammoniated superphosphate always contains large quantities of calcium sulfate, and calcium carbonate in the form of ground limestone is frequently added to mixed fertilizers.

The figures given in Table XI show further that the solubility of tricalcium phosphate was also depressed to a significant extent by the presence of calcium fluoride, monocalcium phosphate, calcium chloride, magnesium carbonate, dolomitic limestone, and precipitated iron and aluminum oxides, and to a less extent by the presence of magnesium sulfate and diammonium phosphate. On the other hand, the solubility of tricalcium phosphate was increased by the presence of ammonium sulfate, monoammonium phosphate, sodium nitrate, potassium chloride, and potassium sulfate. Diammonium phosphate is an alkaline salt, and its effect in decreasing the solubility of tricalcium phosphate is no doubt largely due to an increase in the alkalinity of the citrate solution caused by its presence. Monoammonium phosphate, on the other hand, is an acid salt, and therefore it would be expected that its presence would increase the solubility of tricalcium phosphate. A 0.1 M solution of diammonium phosphate has a pH of 8.0, while a 0.1 M solution of monoammonium phosphate has a pH of 4.4 (21). Neutral alkali salts also seem to have a specific effect in increasing the solubility of tricalcium phosphate. Several investigators (18) have noted that the dissolution of calcium phosphates by water is favored by the presence of alkali metal salts. From the practical standpoint, the effect of water-soluble compounds is probably of no considerable significance, since in the official method of analysis they would be largely removed by washing prior to the citrate digestion.

TABLE XI. EFFECT OF VARIOUS COMPOUNDS ON CITRATE SOLUBILITY OF TRICALCIUM PHOSPHATE 287

(1 gram of $\text{Ca}_3(\text{PO}_4)_2$ plus 1 gram of added material; samples digested for 30 minutes at 65° C.)

ADDED MATERIAL	CITRATE-INSOLUBLE P_2O_5 AS PERCENTAGE OF:		ADDED MATERIAL	CITRATE-INSOLUBLE P_2O_5 AS PERCENTAGE OF:	
	Sample	Total P_2O_5		Sample	Total P_2O_5
None	23.60	57.8	MgCO_3 , ^a	33.89	82.9
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, ^a			synthetic	27.82	68.1
synthetic	30.60	74.9	Dolomite, ^g	26.58	65.1
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, ^a			$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	20.76	50.8
natural	33.74	82.6	$(\text{NH}_4)_2\text{SO}_4$	18.83	46.1
CaCO_3 , ^a			$(\text{NH}_4)_2\text{HPO}_4$	26.87	65.8
synthetic	34.19	83.7	NaNO_3	20.71	50.7
CaCO_3 , ^{a,b}			KCl	20.64	50.5
natural	34.83	85.2	K_2SO_4	20.54	50.3
CaF_2 , ^{a,c}			Fe_2O_3 , ^{a,d}	24.26	59.4
natural	29.44	72.1	Fe_2O_3 , ^{a,e}	28.65	70.1
$\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	29.96	73.3	Al_2O_3 , ^{a,d}	23.65	57.9
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	31.13	76.2	Al_2O_3 , ^{a,f}	27.49	67.3

^a Ground to 100 mesh.

^b High-calcium limestone.

^c Fluorspar, Bureau of Standards, Standard Sample 79.

^d Baker and Adamson's C. P. material.

^e Prepared by treating $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with NH_4OH and drying precipitate on steam bath.

^f Prepared by treating $\text{AlCl}_3 \cdot 12\text{H}_2\text{O}$ with NH_4OH and drying precipitate on steam bath.

^g Containing 33.71 per cent CaO and 17.82 per cent MgO.

The figures given in Table XII show that in the absence of other compounds, 100 cc. of citrate solution dissolved, under the conditions of the experiments, approximately 3 grams of gypsum and of magnesium carbonate, 1.19 grams of calcium carbonate, 0.24 gram of dolomite, 0.05 gram of calcium fluoride, or 0.04 gram of precipitated ferric oxide, the solubility of the last compound depending upon its past history. All these compounds are very much more soluble in citrate solution than in water, owing at least partly, no doubt, to chemical reaction with the citrate. The occurrence of chemical reactions is indicated by the fact that when 3 grams of gypsum are added to 100 cc. of citrate solution at 65° C., the salt dissolves very rapidly and almost completely, but with further digestion a flocculent precipitate forms. This

precipitate is probably calcium citrate and it dissolves almost completely during the final washing with hot water.

TABLE XII. SOLUBILITY OF VARIOUS COMPOUNDS IN NEUTRAL AMMONIUM CITRATE SOLUTION

(Samples digested with 100 cc. of citrate solution at 65° C. for 30 minutes all materials ground to 100 mesh)

MATERIAL	WT. DISSOLVED BY 100 CC. OF CITRATE SOLN.
	Grams
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, synthetic	Approx. 3.0
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, natural	Approx. 3.0
CaCO_3 , synthetic	1.19
CaCO_3 , ^a natural	1.19
CaF_2 , ^b natural	0.05
Dolomite	0.24
MgCO_3 , synthetic	Approx. 3.0
Fe_2O_3 , ^c	0.04

^a High-calcium limestone.

^b Fluorspar, Bureau of Standards, Sample 79.

^c Prepared by treating $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with NH_4OH and drying precipitate on steam bath.

The depressing effect of calcium salts on the solubilities of di- and tricalcium phosphates seems to be due largely to the formation of calcium citrate, thus decreasing the quantity of citrate radical available for reaction with the calcium phosphates. The depressing effect of magnesium compounds and precipitated iron and aluminum oxides is probably due to similar reactions.

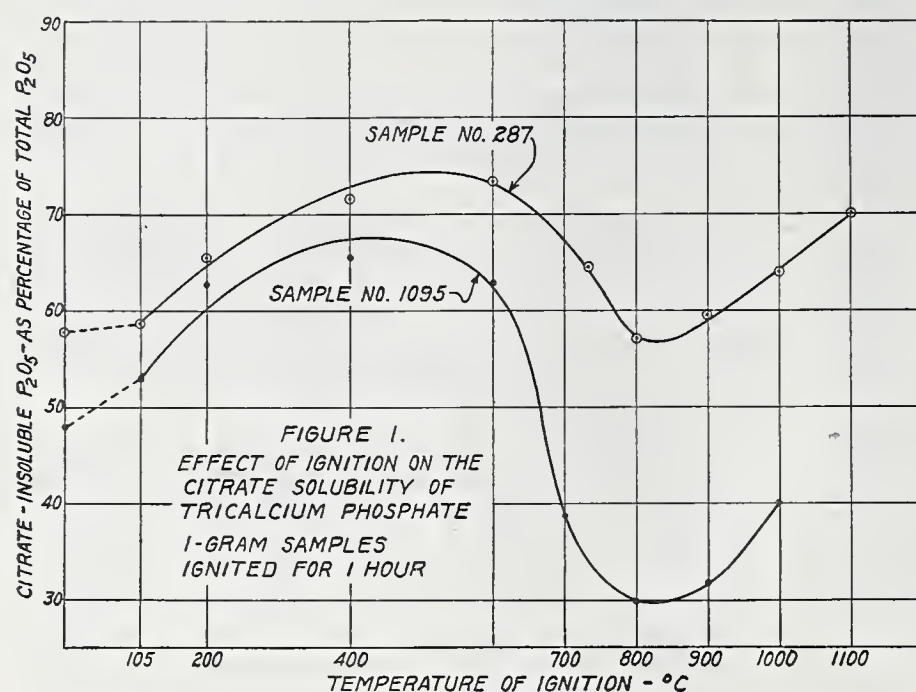
The writers wish to call particular attention to the effect of iron on the solubility of calcium phosphates. A very pronounced greenish yellow color was noted in a citrate solution that had been prepared in an enamel-lined iron kettle, and when this solution was used on tricalcium phosphate much higher figures for citrate-insoluble phosphoric acid were obtained than when a colorless solution prepared in a glass container from the same lot of citric acid was used. The pH values and the specific gravities of the solutions were identical. An analysis showed that 100 cc. of the colored solution contained 0.16 gram of iron calculated as ferric oxide, which, owing to a crack in the enamel, had been dissolved from the kettle, whereas the colorless solution was free of iron. The results given in Table XI indicate that the low solubility obtained by use of the colored solution was due to its iron content. While small quantities of iron in the citrate solution will probably have no effect on the determination of citrate-insoluble phosphoric acid in straight superphosphates and the usual types of mixed fertilizers, only iron-free solutions should be used on tricalcium phosphate, bone products, heavily ammoniated superphosphates, and other difficultly soluble materials.

The foregoing results show that the citrate solubility of tricalcium phosphate in a mixed fertilizer may be considerably lower than that of the same weight of pure salt, not because of a change in the chemical nature of the phosphate but because of the effect of other compounds in reducing its solubility under a particular set of conditions.

EFFECT OF IGNITION

According to Erlenmeyer and Antz (6), air-dried tricalcium phosphate is slightly more soluble in citrate solution than material which has been dried at 50° C., and the latter is much more soluble than material which has been ignited. Barillé (2) states that freshly prepared gelatinous tricalcium phosphate is more soluble than material that has been air- or oven-dried, while the calcined material is insoluble. He also states that hydrated dicalcium phosphate is more soluble than the anhydrous salt, and that this material is rendered insoluble by calcination because of the formation of calcium pyrophosphate. Grupe and Tollens (8) note that citrate solution dissolves significant quantities of tricalcium phosphate if the salt is not dried at too high a temperature. In order to obtain further information on this point, a study

was made of the effect of ignition at various temperatures on the solubilities of di- and tricalcium phosphates. In carrying out these experiments, the desired quantities of material were ignited in platinum dishes at the desired temperature for 1 hour, except those at 105° C. which were heated to constant weight. The individual ignition residues were used for the citrate digestions. Consequently, the results obtained in a series of experiments with a given weight of original material are comparable because the same weight of total phosphoric acid was present in each case.



Pure hydrated dicalcium phosphate, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, theoretically contains 20.93 per cent water of hydration and 5.23 per cent water of constitution, or a total of 26.16 per cent. The material used in the experiments, sample 390, was a very pure crystalline salt containing 0.19 per cent free water in addition to the water of hydration and constitution. Table XIII shows that removal of the water of hydration had a small but definite effect in decreasing the solubility of dicalcium phosphate. When the temperature was raised to 400° C., a portion of the water of constitution was also driven off and the solubility was very greatly decreased because of the formation of calcium pyrophosphate. Previous experiments (12) have shown that less than 10 per cent of the total phosphoric acid in calcium pyrophosphate prepared by igniting dicalcium phosphate at 800° C. is soluble in neutral ammonium citrate solution.

TABLE XIII. EFFECT OF IGNITION ON CITRATE SOLUBILITY OF DICALCIUM PHOSPHATE 390

(Samples digested for 30 minutes at 65° C.)

WT. OF $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ Grams	TEMP. OF IGNITION ° C.	CITRATE-INSOLUBLE P_2O_5 AS PERCENTAGE OF:		LOSS IN WT. %
		Sample	Total P_2O_5	
1.0	...	0.00	0.0	...
1.0	105 ^a	0.06	0.1	3.95 ^b
1.0	200	0.23	0.5	17.91 ^b
1.0	400	24.25	57.3	22.44 ^b
2.0	...	2.33	5.5	...
2.0	105 ^a	5.53	13.1	...
2.0	200	9.70	22.9	...
2.0	400	35.50	83.9	...

^a Heated to constant weight. Total time of heating, 50 hours. Other samples heated for 1 hour.

^b Average of results obtained on 1- and 2-gram samples.

The figures given in Tables XIV and XV show that when tricalcium phosphate was ignited for 1 hour, the percentage of citrate-insoluble phosphoric acid steadily increased up to an ignition temperature of about 600° C. The insoluble phosphoric acid then decreased rather sharply to a minimum at

about 800° C. and increased at higher temperatures. Although the absolute quantities of insoluble phosphoric acid were not the same in the two materials, the curves given in Figure 1 have similar slopes, indicating that the same factors were concerned in the changes in solubility of the two materials. The changes in the solubility of tricalcium phosphate on heating seem to be due principally to changes in the chemical constitution of the material as a result of the loss of water. Somewhat different results would probably be obtained on samples ignited to constant weight at the different temperatures. This point is being investigated further. It will be noted that in the case of tricalcium phosphate, sample 287 (Table XV), small but definite increases in loss of weight occurred as the temperature of ignition was increased from 800° to 1100° C. Bassett (3) has observed that tricalcium phosphate holds water very tenaciously, but he fails to state the temperatures at which his experiments were made.

Unignited tricalcium phosphate passes to a certain extent into the colloidal condition when it is treated with citrate solution, and considerable time is required for filtering and washing the insoluble residue which is finally obtained in the form of a sticky mass. The insoluble material shows no tendency to creep up the sides of the vessel during either the citrate digestion or the washing with hot water. A similar behavior was noted in the case of samples ignited at temperatures up to 400° C. On the other hand, the colloidal and sticky nature of the residues and the time required for filtering and washing progressively decreased, whereas the tendency of the insoluble material to creep up the sides of the vessel increased as the temperature of ignition was in-

TABLE XIV. EFFECT OF IGNITION ON CITRATE SOLUBILITY OF TRICALCIUM PHOSPHATE 1095

(Samples digested for 30 minutes at 65° C.)

WT. OF $\text{Ca}_3(\text{PO}_4)_2$ Grams	TEMP. OF IGNITION ° C.	CITRATE-INSOLUBLE P_2O_5 AS PERCENTAGE OF:	
		Sample	Total P_2O_5
0.5	...	7.14	17.6
0.5	105 ^a	11.34	28.0
0.5	200	15.39	38.0
0.5	400	18.94	46.8
0.5	1000	3.68	9.1
1.0	...	19.48	48.1
1.0	105 ^a	21.43	52.9
1.0	200	25.37	62.7
1.0	400	26.46	65.4
1.0	600	25.42	62.8
1.0	700	15.69	38.8
1.0	800	12.15	30.0
1.0	900	12.88	31.8
1.0	1000	16.20	40.0
2.0	...	26.38	65.2
2.0	105 ^a	29.18	72.1
2.0	200	31.48	77.8
2.0	400	32.36	79.9
2.0	1000	26.50	65.5

^a Heated to constant weight. Other samples heated for 1 hour.

TABLE XV. EFFECT OF IGNITION ON CITRATE SOLUBILITY OF TRICALCIUM PHOSPHATE 287

(1-gram samples digested for 30 minutes at 65° C.)

TEMP. OF IGNITION ° C.	CITRATE-INSOLUBLE P_2O_5 AS PERCENTAGE OF:		LOSS IN WT. %
	Sample	Total P_2O_5	
...	23.60	57.8	...
105 ^a	23.97	58.7	1.94
200	26.81	65.6	2.73
400	29.18	71.4	4.21
600	30.01	73.4	5.77
700	26.39	64.6	5.99
800	23.33	57.1	6.23
900	24.35	59.6	6.38
1000	26.17	64.0	6.58
1100	28.56	69.9	6.63

^a Heated to constant weight. Total time of heating, 40 hours. Other samples heated for 1 hour.

creased from 400° to 1100° C. The extracts from samples ignited at 1000° and 1100° C. filtered very rapidly and the insoluble residues had practically no colloidal and sticky properties.

A comprehensive investigation of the constitution and properties of tricalcium phosphate and the complex calcium phosphates is now being made in the Fertilizer Technology Division of the Bureau of Chemistry and Soils.

ACKNOWLEDGMENT

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Analysis of Beryllium Minerals

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ALTHOUGH beryllium was discovered by Vauquelin in 1798, neither the metal, its minerals, nor its compounds have found any use in industry or the arts until quite recently. However, it has attracted considerable scientific interest since its discovery. Questions regarding its physical and chemical properties, its compounds, and methods of separation have received much attention and the answers have been found only after much study.

In making beryllium analyses the preliminary work offers no difficulties. It consists of a sodium carbonate fusion and the separation of silica in the usual way, then precipitation of the hydroxides with ammonia. This precipitate will carry the beryllium as hydroxide, together with iron, alumina, etc. As beryllium hydroxide is appreciably soluble in water, all washing should be done with a 2 per cent solution of ammonium nitrate.

In analyzing phosphate minerals, phosphorus must be separated as ammonium phosphomolybdate before proceeding with the other separations. The solution of the hydroxides in hydrochloric acid may be treated with hydrogen sulfide if second-group metals are present before proceeding with the other separations, but this is probably never necessary in ordinary mineral analysis.

In the author's work on the minerals mentioned above, three methods for the separation of aluminum and iron were used, beryllium in all cases being finally precipitated as the hydroxide with ammonia, and weighed as beryllium oxide after ignition.

METHOD OF BERYLLIUM DEVELOPING CORPORATION

H. S. Cooper, of the Beryllium Development Corporation of Cleveland, Ohio, reported (in a private communication to the author) a method which consists briefly in igniting the mixed hydroxides, fusing with sodium carbonate, leaching the melt with water, filtering, and then repeating the ignition, fusion, and leaching. Generally this second fusion and leaching will remove the last of the alumina, but with minerals high in

alumina a third fusion may be necessary. The last residue is ignited and fused with potassium pyrosulfate and dissolved in water. This should give a clear solution, except perhaps for a little silica which is removed by filtration. From this solution the hydroxides of iron and beryllium are precipitated with ammonia and collected on a filter, dissolved in dilute hydrochloric acid, and again precipitated with ammonia. The solution and re-precipitation are necessary to free the precipitate from alkali salts, which are readily adsorbed by beryllium hydroxide.

The precipitate is ignited and weighed as beryllium oxide and ferric oxide. The precipitate is then dissolved in hydrochloric acid, the iron determined, and beryllium oxide found by difference.

This method is obviously open to the criticism that obtaining the beryllium percentage by difference throws all the errors on the beryllium. Still it is a very satisfactory technical scheme.

Another objection is that the method as outlined takes no account of manganese, which is a common constituent of beryllium minerals. If neglected, it is very largely carried through all the operations and will be reported as beryllium oxide.

Manganese may be separated as follows: After making the bisulfate fusion, dissolving in water, and precipitating the hydroxides with ammonia, filter and dissolve the hydroxide precipitate with dilute nitric acid back into the beaker in which the precipitation was made. Evaporate to a small volume, but not to dryness, add 10 cc. of concentrated nitric acid, and precipitate the manganese with potassium chlorate. Filter out this precipitate and from the filtrate separate the iron and beryllium with ammonia as described above.

This separation for manganese is never quite complete, so that traces of manganese will still be found with the beryllium. This small amount can be determined colorimetrically and deducted if necessary. With small amounts of manganese, oxidation sometimes goes to the permanganate condition.

and this has been overcome by pouring the solution through the filter paper several times, thereby reducing permanganate to manganese dioxide.

It is claimed that when precipitating alumina with ammonia the precipitate can be kept free from manganese by careful regulation of the alkalinity. Hillebrand and Lundell (1) recommend the use of a few drops of methyl red (0.02 per cent alcoholic solution) for an indicator and the addition of dilute ammonia drop by drop until the color changes to a distinct yellow, then boiling the solution for not more than 2 minutes. The solution should contain at least 5 grams of ammonium chloride for each 200 cc. of solution. Aluminum hydroxide is completely precipitated between pH 6.5 and 7.5. The transition range of methyl red is given as pH 4.2 to 6.3 (1).

As beryllium hydroxide resembles aluminum hydroxide in its behavior with ammonia, it is perhaps possible that manganese may be separated from beryllium in this way, but in this laboratory the separation has never been quite complete.

PARSONS' METHOD (3)

In this method the mixed hydroxides obtained in the usual manner are dissolved in dilute hydrochloric acid and the solution nearly neutralized by the careful addition of ammonia. To the slightly acid solution 10 grams of sodium bicarbonate are added, the solution diluted with water to 100 cc., brought quickly to the boiling point, and boiled for 30 seconds. The precipitate is filtered and washed with a warm 10 per cent solution of sodium bicarbonate. The precipitate is dissolved in warm dilute hydrochloric acid, nearly neutralized with ammonia, and the precipitation repeated with sodium bicarbonate. It is filtered and washed as before. To the combined filtrates 5 to 10 cc. of colorless ammonium sulfide are added, the mixture is stirred well and allowed to stand cold until the iron precipitate coagulates and settles, then it is filtered and washed.

The filtrate is made slightly acid by the careful addition of hydrochloric acid, the carbon dioxide boiled off, ammonia added until slightly alkaline, and the mixture boiled. Beryllium is precipitated as beryllium hydroxide. This is collected on a filter, washed with 2 per cent ammonium nitrate solution, ignited, and weighed as beryllium oxide.

When working on proof material, this method always gives results somewhat high, owing to incomplete separation of alumina together with manganese if this is present. With the small amount left with the beryllium, manganese is best determined colorimetrically and deducted from the final weight.

The alumina left with the beryllium can be separated by the use of 8-hydroxyquinoline.

8-HYDROXYQUINOLINE METHOD

The separation of aluminum from beryllium by the use of 8-hydroxyquinoline is described in an article by Lundell and Knowles (2). From a solution slightly acid with acetic acid, 8-hydroxyquinoline precipitates aluminum completely, leaving beryllium in solution. After removal of the aluminum by filtration, beryllium is precipitated as the hydroxide by careful addition of ammonia, after which it is filtered, ignited, and weighed.

This is probably the sharpest separation available for these two elements. The only objection is that the aluminum precipitate with 8-hydroxyquinoline is very bulky. In the application of this method to ores which are usually fairly high in alumina, a precipitate is obtained which is somewhat troublesome to handle. As iron in the ferric condition accompanies this precipitate, the bulk is increased still more. With such large precipitates at least one re-solution and re-

precipitation is necessary, and this results in a large volume of solution from which to separate beryllium. Here again manganese is not completely precipitated.

For this reason it has been found more satisfactory to combine the 8-hydroxyquinoline separation with the Parsons method. That is, after making the bicarbonate precipitations, separating the iron, and acidifying the filtrate, to the slightly acid solution is added an excess of a 2.5 per cent solution of 8-hydroxyquinoline in acetic acid, followed by 20 or 25 cc. of saturated ammonium acetate solution. The precipitate is allowed to settle, filtered, and washed with cold water.

To the filtrate, a slight excess of ammonia is added, the mixture boiled, filtered, the precipitate washed with 2 per cent ammonium nitrate solution, ignited, and weighed as beryllium oxide.

If manganese is present in the ore, more or less will be found with the beryllium oxide. This can be determined colorimetrically and deducted or, if too much is present for a colorimetric determination, it should be precipitated from a nitric acid solution with potassium chlorate.

This procedure gives the best direct determination for beryllium for technical purposes.

The accurate determination of small percentages of beryllium is a difficult problem. If a large quantity of the material is used, say 5 grams, the removal of the large amount of silica is troublesome. Besides, this usually means the presence of a relatively large amount of alumina, which adds to the difficulties.

There are few, if any, really distinctive qualitative tests for either aluminum or beryllium, hence it is not possible to test qualitatively for complete separations during the analysis.

Kolthoff claims that as little as 0.05 mg. of beryllium per liter can be detected with curcumin. Curcumin is adsorbed by beryllium hydroxide, giving a reddish color to the precipitate. Iron and aluminum both interfere, but it is claimed that the addition of sodium fluoride to the solution will overcome their influence.

Working with a proof solution fairly good results with this reagent were obtained but, working with minerals, results were very poor on account of the color fading rapidly.

It is quite possible that the poor results are due to faulty technic, but so far the difficulty has not been located.

The retention of beryllium in the silica no doubt needs attention. We know that silica retains a little alumina, which is recovered after volatilizing the silica with hydrofluoric acid. It seems probable that a little beryllium is also retained and in a very careful analysis this should receive attention.

The following tabulation shows a comparison of results obtained on minerals using different methods, and also recovery on proof material:

	BERYLLIUM CORP. METHOD		PARSONS + QUINO- LINE	QUINO- LINE
	Mn not separated	Mn separated		
Standard pulp 7.8% BeO	8.3	7.7	7.83	8.00 8.10
Proof solution 0.077% BeO			0.081 0.077 0.075	0.07
Beryl specimen		12.6	12.6 12.8	

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Rapid Method for Determination of Sulfur in Brass and Bronze

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THE following method of analysis is one developed by the necessity of rapidly determining the sulfur content of phosphor bronze-bearing metals, the usual method of removing the metals by solution in nitric acid and electrolysis being too time-consuming for use in this case.

The method depends on the solution of the sample in cupric ammonium chloride and the consequent precipitation of the sulfur as metallic sulfide, which is filtered off, oxidized, and the sulfur precipitated in the usual manner with barium chloride. The method has the advantage, other than saving time, of being indifferent to the amount of sulfur contained in the sample, whereas, in the regular method referred to above, it has been noted that in cases of unusually high sulfur content, some of the sulfur escapes oxidation and floats on the surface in elemental form and will be lost if extraordinary precaution is not taken.

The method may be adapted to materials other than brass or bronze, the only limiting factor being the possibility of dissolving the metal in the reagent used. Metals below copper in the electrochemical series will, of course, not dissolve and will be precipitated with the sulfur and, if present in any considerable amount, will cause trouble in the subsequent operations. Antimony up to as high as 5 per cent does not interfere seriously, and amounts larger than this are rarely met with in brass or bronze.

The solution used can be regenerated with chlorine gas in the same manner as that used for carbon determinations in steel. It is not necessary to run a blank on the solution if it is filtered before use, although blanks should be run on the other reagents used.

SOLUTION REQUIRED. Cupric ammonium chloride ($\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$). One part of the salt to 3 parts of water and 5 per cent of hydrochloric acid added. Use in the proportion of 12 grams of salt to 1 gram of metal.

METHOD. Dissolve 5 grams of the brass or bronze, as finely divided as possible, in the required amount of solution, using gentle heat and stirring the solution occasionally. When everything is in solution except the gray to black sulfide residue and any traces of carbon, antimony, bismuth, etc., that may be present, remove from the heat and let stand for a few minutes. Do not allow to cool before filtering, for lead chloride may precipitate. Filter on a sulfur-free asbestos mat, using suction, and remove the main portion of the filtrate before washing so as not to dilute the cupric solution unnecessarily before regeneration. Wash the mat and residue with 5 per cent hydrochloric acid and then with water, and remove the mat to a 400-cc. Pyrex beaker, using as little water as possible to wash out the last traces of precipitate. Add concentrated nitric acid equal to the amount of water in the beaker, then 10 cc. of saturated bromine water, and boil until the bromine is expelled. The nitric acid will dissolve any metallic residues in the precipitate and set free any sulfur that may be occluded by them.

After the bromine is expelled, dilute with an equal volume of water and filter rapidly from the asbestos fiber, a piece of absorbent cotton being convenient for this filtration. Add about 0.5 gram of sodium bicarbonate to the filtrate, heat to dryness, bake to remove the nitric acid, and dehydrate any silica that may have dissolved from the asbestos. Dissolve in 5 cc. of hydrochloric acid and 25 cc. of water, bring

to a boil, and filter from siliceous matter, washing the filter paper with hot 5 per cent hydrochloric acid. The sulfur is precipitated as barium sulfate in the filtrate, with a 10 per cent solution of barium chloride.

If the brass is heavily leaded or contains more than traces of antimony, it is best to add sufficient c. p. granulated zinc to the solution before filtering from the siliceous matter. This will precipitate all the heavy metals and they will be filtered off with the siliceous matter.

Samples of Bureau of Standards phosphor bronze No. 63, recommended sulfur value 0.06, gave the following results by the above method: 0.063, 0.063, 0.066, 0.062, and 0.067. The same standard with 0.2 gram of antimony metal added to each determination gave the following: 0.060, 0.065, 0.061, and 0.059.

Samples of 50-50 lead-copper piston-packing metal analyzing 0.40 per cent sulfur by carefully controlled electrolytic methods gave by this method 0.426, 0.434, 0.436, 0.430, and 0.427.

The method has been in continual use in this laboratory for about six months and has been entirely satisfactory. The time required from the weighing of the sample to the precipitation of the sulfate is less than one hour and is so arranged that the barium sulfate is allowed to settle overnight. The important feature in this case is that the electrolytic apparatus is free for use in the remainder of the analysis, and one man can carry along all determinations simultaneously.

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Corrosion Test on Casing-head Gasolines

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THE A. S. T. M. requirement for corrosion test is that a copper strip shall be immersed in the gasoline in a test tube and maintained at 122° F. (50° C.) for 3 hours. The following short method has been used in this laboratory:

To 10 cc. of gasoline in a test tube add two drops of mercury and shake. If no black precipitate of mercury sulfide is formed, and if the surface of the mercury remains bright, the corrosion test will be negative. If a black precipitate is formed, the regular A. S. T. M. test should be made.

Most casinghead gasolines and some straight-run gasolines contain practically no sulfur, and the above test verifies negative corrosiveness for routine samples.

This test, of course, does not apply to cracked gasolines, refinery absorption gasoline, or other comparatively high-sulfur gasolines.

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Impurities in White Sugar

IV. Determination of Nitrogen

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IN INVESTIGATIONS of the effects of non-sugars on the properties of sugars and sugarhouse products, attention has long been focused on the various forms of nitrogen which may be present (5, 10, 13, 15, 18, 20, 26, 27). Inorganic and organic compounds of this element are present in the raw materials entering into the manufacture of white sugars, and while the clarification (defecation) processes are designed to remove the nitrogenous organic substances as completely as possible, no commercially feasible method of completely eliminating them from the juices (23) has been found. Even in the refinery they are not completely removed from the liquors (1). Neither are the inorganic nitrogen compounds completely removed by bone-char refining (14).

Methods of estimating the various types of nitrogen compounds in juices, sirups, and molasses have been extensively studied by many investigators, and it is now possible, in such lower purity sugarhouse products, to determine total nitrogen (16, 20), ammonia (4, 26), amido nitrogen (4, 27), amino acid nitrogen (10, 27), protein nitrogen (10, 24, 26), betain nitrogen (19, 20, 21), nitrates (17, 25), and nitrites (2, 25). Such a thorough partition of the nitrogen in white sugars, however, is not possible at present on account of the extremely small quantity of the total nitrogen in the sugars. It is possible, by using the methods described in the following paragraphs, to determine total nitrogen, protein nitrogen, amino acid nitrogen, ammonia, nitrates, and nitrites in white sugars. The samples of sugar used for the analyses here reported comprised various commercial grades of refined cane, of plantation granulated cane, and of granulated beet sugars.

TOTAL NITROGEN

An excellent method for the determination of nitrogen in low-purity products by micro-Kjeldahl technic has been described by Stanek and Vondrak (20), but it is not convenient nor economical to submit to Kjeldahl digestion sufficient white sugar to yield enough ammonia for even a microtitration. Hence resort was had to a Kjeldahl digestion on smaller amounts of sugar, followed by estimation of the ammonia in the distillate by means of Nessler's reagent. But here it was found necessary to modify the Kjeldahl technic because it was impossible to procure potassium sulfate sufficiently free from nitrogen.

REAGENTS

AMMONIA-FREE WATER. I. What will hereafter be called "ammonia-free" water is prepared by boiling distilled water with very finely powdered magnesium oxide until the distillate gives no test with Nessler's reagent, and the water, which subsequently distills, is collected in ammonia-free containers. (Magnesium oxide was used here in preference to the more usual sodium hydroxide or carbonate because its suspensions boil more evenly if the oxide is very finely divided. For this purpose the finest powdered oxide obtainable is necessary, that which will pass in

TOTAL nitrogen in white direct-consumption sugars has been determined by a Kjeldahl digestion of the sugar followed by nesslerization of the distillate. The nitrogen so found includes that present as nitrates in the sugar.

Protein nitrogen has been determined by precipitating the protein as tannate and determining the nitrogen in the precipitate by the same method as used for total nitrogen. Alpha amino acids and related compounds have been determined by ninhydrin. Nitrates have been determined by reduction with Devarda's alloy to ammonia followed by distillation and nesslerization of the distillate. Nitrites have been determined by Ilosvay's modification of Peter Griess' colorimetric test.

suspension through a 150-mesh screen.) The whole distillation must be carried out in an atmosphere free from ammonia and its volatile compounds, or in a closed system. The ammonia-free water so obtained is used for the preparation of the standard ammonium chloride comparison solutions and for aliquoting the distillate when necessary before nesslerization.

II. What will hereafter be referred to as "magnesia water" is prepared by concentrating to two-thirds or one-half its original volume a suspension of the finely powdered magnesium oxide in distilled water. It is allowed to cool and settle in an ammonia-free atmosphere. The clear or slightly turbid supernatant magnesia water is suitable for use as ammonia-free water in making solutions and in diluting solutions before distillation. It cannot be used for diluting

a solution to which Nessler's reagent is to be added.

COPPER OXIDE. Powdered copper oxide is ignited to a bright red heat to burn off all nitrogenous matter. It is cooled and stoppered closely to exclude ammonia and the condensation of ammonium salts from the air.

SULFURIC ACID. Pure concentrated sulfuric acid of specific gravity 1.84 is used.

POTASSIUM HYDROXIDE SOLUTION. A solution containing 200 grams of potassium hydroxide (stick form) per liter is prepared with magnesia water.

SODIUM HYDROXIDE SOLUTION. A saturated solution of sodium hydroxide (stick form) in magnesia water is prepared.

NESSLER'S REAGENT (22).

STANDARD AMMONIUM CHLORIDE SOLUTION. Exactly 1.9093 grams of pure ammonium chloride are dissolved in 1 liter of ammonia-free water. Of this solution, 20 cc. are diluted to 1 liter with ammonia-free water. The resulting solution contains 0.01 mg. of nitrogen as ammonia in each cubic centimeter.

APPARATUS

The apparatus used was a regular Kjeldahl digestion and distillation outfit and ordinary 100-cc. Nessler tubes. Before each determination, the stills must be freed from nitrogen compounds by distilling a suspension of the finely powdered magnesium oxide in distilled or magnesia water until no color develops when 2 cc. of Nessler's reagent are added to 100 cc. of the distillate. This may take some time when the apparatus is first set up. Any rubber stoppers or connections should be boiled out thoroughly with dilute sodium hydroxide solution before they are used. If the apparatus must be in a room where other chemical work is being carried on, it is necessary to perform all distillations in a closed system and, when not in use, to protect the stills and condensers from nitrogenous fumes.

METHOD

Kjeldahl flasks of 800 cc. capacity were cleared of ammonia by concentrating to one-half its volume at least 600 cc. of magnesium oxide suspension. The residual suspension in the flasks was discarded, and the unrinsed flasks were immediately used for the digestion. Ten cubic centimeters of a magnesia water solution, containing 10 grams of sugar per 100 cc., were pipetted into the flask. (In analyzing sugars which are low in total nitrogen, larger quantities of the sugar should be taken. Two and five-tenths grams of the dry sugar were used for the analyses of this type of sugar in this investigation.) To this were added about 1 gram of copper oxide powder from the tip of a spatula, 25 cc. of concentrated sulfuric acid, and, very cautiously, 25 cc. of the potassium hydroxide solution. The mixture was cautiously heated with a small flame until frothing ceased and then with a strong flame until the carbon was completely oxidized and

the solution was of a clear green color. The digestion was completed in about 2 hours. After the mixture had cooled, it was diluted with 400 cc. of magnesium water and made alkaline with 50 cc. of the saturated sodium hydroxide solution. A teaspoonful of the finely powdered magnesium oxide was added at the same time. The flask was immediately connected with the still and 200 cc. of distillate were collected. This operation must also be carried out in an ammonia-free atmosphere or in a closed system. To each 100 cc. of distillate 4 cc. of Nessler reagent were added as in ordinary water analysis, and after 15 minutes the colors which had developed were compared with those which had developed simultaneously from known quantities of the standard ammonium chloride solution diluted to 100 cc. with ammonia-free water.

An alternative method of measuring the ammonia obtained, which is not only convenient but economical if a large number of analyses are to be made, is to compare the color of the nesslerized solutions in a spectrophotometer against distilled water. The transmittancy (T) at 510 $m\mu$ of each of a series of nesslerized solutions containing known and differing quantities of ammonium chloride was determined within 15 to 45 minutes after the addition of the reagent. If the transmittancy is expressed as a decimal and the logarithm of its reciprocal ($\log 1/T$, or $-\log T$) is plotted as ordinate against the quantity of nitrogen as ammonia in each solution as abscissa, a straight line is obtained which has a slope corresponding to an increase of 0.0530 in the $-\log T$ value for each increment of 0.01 mg. of nitrogen. The line as plotted does not pass through the origin, but a little above it, depending on the depth of color of the Nessler reagent itself. Hence the position of the line on the graph must be determined with each new batch of Nessler reagent used. From the line so obtained, the quantity of nitrogen in an unknown is readily and easily determined by finding the $-\log T$ value of the nesslerized distillate, without the necessity of making up new standard solutions for each set of determinations.

The results obtained by either method of measurement, after deducting the quantity of nitrogen as ammonia which was present in the reagents and which was determined by a blank determination on the reagents without sugar, were calculated to parts per million of sugar. The nitrogen content of sugars representative of many studied by this method is given in Table I.

The nitrogen obtained by this method includes that present as nitrates. This was demonstrated by making determinations on a series of four solutions of nitrate-free sugar to which were added before the Kjeldahl digestions 0.0, 10, 20, and 40 micro-milligrams of nitrogen as potassium nitrate. There were recovered 0.0, 10, 17, and 39 micromilligrams of nitrogen, respectively.

PROTEIN NITROGEN

The protein nitrogen in juices has been extensively investigated by Vondrak and others (10, 24, 26). The amount of protein in white sugars is generally so small that it is impossible to obtain a definite color test with protein reagents or to obtain more than a turbidity with such protein precipitants as copper sulfate, mercuric nitrate, phosphotungstic acid, and tannic acid. In two unusual sugars, sufficient protein was present to yield a biuret test when the precipitate obtained with copper sulfate was collected on a filter paper and moistened with a little dilute sodium hydroxide solution. When analyzed for protein nitrogen by the method to be described, the one giving the stronger biuret test was found to contain 8.6 parts per million of protein nitrogen.

REAGENTS

Prepare the same reagents as were used for total nitrogen and also

TANNIC ACID SOLUTION. Ten grams of tannic acid are dissolved in distilled water and made up to 100 cc.

METHOD

According to Vondrak (26), the tannic acid method of determining protein in the presence of sugar is the most accurate. To a solution of 25 grams of the sugar in 100 cc. of water, 5 cc. of the tannic acid solution were added. After the mixture had been heated on the steam bath for 2 hours to facilitate coagulation of the precipitate, it was filtered on a quantitative filter paper. The paper and the precipitate were washed free from sugar with ammonia-free water, placed in an 800-cc. Kjeldahl flask, and analyzed for nitrogen by the method described above

for total nitrogen. Blanks were determined on a similar solution of protein-free sugar. The quantity of nitrogen found in these blanks was deducted from that found in the tannic acid precipitate, and the result was calculated to parts per million. The quantity of protein nitrogen in the representative sugars is shown in Table I.

TABLE I. NITROGEN IN WHITE GRANULATED SUGARS

SAMPLE	TOTAL N	PROTEIN N	AMINO ACID N	N AS NH ₃	N AS NO ₃ ⁻	N AS NO ₂ ⁻
	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.
1	35	0.3	3.5	0	4	0.004
2	45	3.9	4.0	0	8	0.004
3	5	0.0	0.0	1	5	0.0
4	10	1.0	5.5	2	4	0.014
5	33	0.8	5.5	0	8	0.024
6	45	1.5	1.0	2	30	0.0
7	7	0.0	0.0	2	2	0.020
8	23	4.4	..	2	0	0.0
9	64	0.4	5.0	1	3	0.002
10	24	0.3	0.0	2	10	0.003
11	20	2.8	5.0	0	6	0.001
12	5	0.5	2.5	0	6	0.0
13	13	0.4	0.0	2	8	..
14	52	1.3	7.5	4	14	0.002
15	25	4.1	4.0	0	10	0.004
16	82	1.2	10.0	2	8	0.003
17	36	2.3	5.0	4	10	0.003
18	17	0.0	0.0	2	2	0.249
19	26	0.3	0.0	2	0	..
20	55	1.2	5.0	4	10	0.099
21	72	6.8	7.5	2	14	0.009
22	85	8.4	6.0	2	12	0.049
23	30	2.4	5.0	2	8	0.001
24	22	0.9	5.0	4	12	0.001
25	17	4.6	4.0	0	10	0.001
26	186	2.1	10.0	12	12	0.001
27	7	0.0	0.0	2	2	0.007
28	33	2.4	7.5	6	10	0.001
29	30	4.8	8.0	6	8	0.039
30	4	0.0	0.0	1	2	0.0
31	16	1.4	3.5	0	8	0.014
32	18	0.0	2.5	6	8	0.001

AMINO ACID NITROGEN

The amino acid nitrogen content of the sugars was determined by the ninhydrin method (1, 9). This test, it must be remembered, is not specific for amino acids but is given by compounds having an amino group in the alpha position to a carboxyl group. The quantity of nitrogen present in this atomic grouping in the representative white sugars is shown in Table I.

Some sugars when treated with ninhydrin give a color which is redder than that of the standard solutions containing aspartic acid. This is due to the fact that different amino acids produce slightly different tones of purple, that given by aspartic acid representing the most commonly encountered color. The reddish nuance causes some difficulty in matching the colors of the solutions, but satisfactory approximations are possible.

The fact that proteins themselves respond to this test does not mean that the results found by this method must be greater than those found in the tannic acid-protein method, which shows the total nitrogen in the protein. Only a small proportion of the total nitrogen in any protein is present in the grouping, $R.CH(NH_2).COOH$, which reacts with ninhydrin. Nitrogen in other groupings is inactive. Of the amino acids themselves, proline and oxyproline, containing no alpha amino groups, do not respond to the test. Tryptophane, which contains, besides the active grouping, nitrogen bound in a ring, reacts for only one-half its total nitrogen, and arginine and histidine similarly would show only one-third of their total nitrogen. These facts must be borne in mind in interpreting the values found by this method, which is specific for no individual compound but is characteristic for an atomic grouping occurring in varying proportions in many compounds.

AMMONIA AND NITRATES

The determination of ammonia in low-purity products has been thoroughly worked out by Baerts and Delvaux (4) and

by Vondrak (26), who have shown that the true value for ammonia may be obtained by distilling with magnesium oxide at 40° to 50° C. under reduced pressure. If the distillation is carried out at atmospheric pressure, the amides present are hydrolyzed to ammonia even by magnesium oxide. In white sugars, the ammonia present is so small that it was not deemed practical to use reduced pressure for the distillation. In fact, the values given in Table I for ammonia are really the values of blanks for the nitrate determinations, representing the nitrogen from all compounds present which yield ammonia when treated with alkali under the conditions obtained during the determination of nitrates. Of the various methods of determining nitrates, the only feasible one in which the large excess of sucrose does not interfere is that in which the nitrates are reduced to ammonia. The reducing agent chosen was Devarda's alloy (6, 8), and the method of reduction was essentially the same as that used by Chibnall (7).

REAGENTS

MAGNESIA WATER. This is prepared as described under "Total Nitrogen."

SODIUM HYDROXIDE SOLUTION. A solution containing 400 grams of stick sodium hydroxide per liter is prepared with magnesia water.

DEVARDA'S ALLOY. The best grade of alloy is ground fine enough to pass through a 50-mesh screen.

NESSLER'S REAGENT (22).

STANDARD AMMONIUM CHLORIDE SOLUTION. The standard solution is prepared as described under "Total Nitrogen."

METHOD

Two and five-tenths grams of sugar were dissolved in 250 cc. of magnesia water in an 800-cc. Kjeldahl flask. One gram of powdered Devarda's alloy, 50 cc. of the sodium hydroxide solution, and a teaspoonful of the finely powdered magnesium oxide were added, and the flask was immediately connected to the distillation apparatus. At the same time a similar solution was prepared without the alloy and connected to the still. After they had stood at ordinary temperature for at least 30 minutes and the vigorous evolution of hydrogen had subsided, the mixtures were slowly heated to boiling and distilled as in the determination of total nitrogen, until 200 cc. of distillate had been collected in Nessler tubes. The ammonia in the distillate was determined colorimetrically and corrected for ammonia and nitrates in the reagents as found in blank determinations carried out without sugar. The amount of nitrogen as ammonia in the distillate from the mixture to which no alloy had been added represents the nitrogen as "ammonia" in the sugar. When this quantity is deducted from that found in the distillate from the mixture to which the alloy had been added, the difference is the nitrogen as nitrate in the sugar. Although Devarda's alloy reduces nitrites as well as nitrates, and therefore the nitrate value so found is really the sum of the nitrate and the nitrite nitrogens, no further correction is generally necessary, since the nitrite nitrogen is such a small quantity (see Table I).

When Nessler's reagent is added to these distillates, a greenish color is generally formed, due to volatile organic substances formed by the action of the alkali on the sugar. (A similar color is formed when Nessler's reagent is added to a dilute solution of alcohol.) This coloration does not interfere with the development of the color due to ammonia, but its presence in the solutions precludes the measurement of the colors spectrophotometrically. If, however, both the standard ammonium chloride tube and the unknown tube are viewed through a Wratten K-3 No. 9 yellow light filter, the interference is overcome for colorimetric comparison and perfect matching is possible.

The quantities of ammonia and of nitrates in the representative sugars as determined by these methods are shown in Table I.

NITRITES

The presence of nitrites in sugar-beet products has been ascribed by Urban (25) to the introduction of oxides of nitrogen with the carbon dioxide used for carbonation. In the burning of limestone in kilns for the production of lime and carbon dioxide, a small quantity of nitrogen is unavoidably fixed as oxides which are absorbed by the alkaline juice along

with the carbon dioxide and give rise to nitrites. Urban determined them in the juices by reduction with Devarda's alloy. This method is not feasible with white sugars because the quantity of nitrites present is so small. The same objection holds in regard to the gasometric method used by Pellet (12) and by Andrlik and Stanek (2). However, when analyzing white sugar, conditions are ideal for the use of Ilosvay's modification of Peter Griess' extremely sensitive colorimetric test (11), which, of course, cannot be used with colored sugars and juices. Since this test is slightly less sensitive in the presence of sucrose the standard comparison solutions must contain the same concentration of sucrose as the unknowns.

The reagents, sulfanilic acid and alpha-naphthylamine hydrochloride solutions, and the standard nitrite solution were prepared according to the directions recommended by the Association of Official Agricultural Chemists (3). The tests were made on solutions containing 20 grams of sugar in each 100 cc., after objectionable turbidity had been removed by filtration with Filter-Cel. The comparison solutions were made from a similar solution of nitrite-free granulated sugar, to which known volumes of the standard nitrite solution were added. After 2-cc. portions of each reagent had been added to 100 cc. of each known and unknown solution in Nessler tubes, the solutions were thoroughly mixed, allowed to stand at room temperature for at least 30 minutes, and then compared colorimetrically. If, as rarely happens, the color of the unknown is tinged with yellow or brown, the color of the standards may be given a similar hue by the addition of a few drops of a very dilute caramel solution.

As shown in Table I, the quantity of nitrites in white sugars is generally very small.

ACKNOWLEDGMENT

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Interference of Reducing Sugars in Ninhydrin Reaction for Amino Acids and Related Compounds as Applied to Carbohydrates

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IN ATTEMPTING to apply the ninhydrin reaction for amino acids (1) to some samples of honey it was noted that, although one of the honeys showed a deep blue color soon after the reaction mixture was placed in the boiling-water bath, at the end of the half-hour reaction period the mixture was deep brownish red, and on diluting it for the measurement, no trace of the characteristic violet color was to be found. The transitory blue color was not observed in the other samples of honey being tested, and in no case was a positive test for amino acids obtained. Because of this it seemed advisable to study the effect of *d*-glucose and of *d*-fructose on the reaction.

In the previous study of the application of this reaction to sugars and sugarhouse products (1), it was found that 4 mg. of *d*-glucose per cc., or a total of 8 mg. in the reaction mixture has no effect on the reaction. The effect of increasing proportions of both *d*-glucose and *d*-fructose has now been studied, and the results obtained are given in Table I.

TABLE I. EFFECT OF INCREASING PROPORTIONS OF REDUCING SUGAR IN NINHYDRIN REACTION

REDUCING SUGAR	WT. TAKEN		NITROGEN TAKEN		REMARKS
	Mg.	Mg.	Mg.	Mg.	
<i>d</i> -Glucose	10	0.02	0.02		No interference
	20		0.02+		Slightly redder and darker than standard
	50				Redder and darker still
	80				Redder and darker still
	100				Redder and darker still
	150				Lighter than preceding and muddy
	200				Lighter than preceding and muddy
<i>d</i> -Fructose	400				Much lighter and muddy
	500				Pale muddy violet
	1	0.01	0.01+		Slightly redder than standard
	2		0.01+		Slightly redder than standard
	3				Redder and darker than preceding
	4				Redder than preceding
	5				Redder than preceding
	6				Redder than preceding
	7				Redder than preceding
	8				Redder than preceding
	9				Red-violet
	10	0.02			Redder and darker than standard
	20				Redder and darker still
	50				Similar to 500 mg. of glucose
	80				Muddy yellow
	100				Paler muddy yellow
	150				Still paler muddy yellow
	200				Light orange
	400				Darker orange
	500				Deeper orange
	400	0.20			Very dark brown (see text)
Glucose + fructose (1 to 1)	4 to 20	0.01			Same colors as with fructose 2 to 10 mg.

The indicated amounts of the two sugars were weighed into clean test tubes with sufficient amino acid-free granulated sugar to give a total weight of 1 gram of total sugars. The sugars were then dissolved in 2 cc. of a solution of aspartic acid of known concentration, and the reaction mixture was

completed as usual with 2 cc. of the phosphate buffer solution (pH 6.9) and 1 cc. of ninhydrin solution. For comparison, 1 gram of the sucrose was similarly dissolved in aspartic acid solution and made up with the buffer and ninhydrin solutions. All the tubes were heated for one-half hour, and the colors produced were noted every 5 minutes.

From these experiments it is evident that reducing sugars are objectionable in the ninhydrin test when more than 10 mg. of glucose or 1 mg. of fructose are present. The greater activity of fructose was further shown by the fact that all the tubes containing this sugar, with the exception of the one containing 1 mg., developed a red color during the first 5 minutes of heating, whereas the tubes containing glucose, after being heated for 10 minutes, showed merely a gradation of purple corresponding to the quantity of glucose present, and the one with 10 mg. was still purple when removed from the bath at the end of half an hour.

The experiment with 400 mg. of fructose and 0.20 mg. of nitrogen was watched more carefully than the others. In less than 2 minutes after it was placed in the bath it had developed a deep blue color. In about 15 minutes slight effervescence was noted, and the blue color gradually disappeared until in 25 minutes the color was a deep red. When diluted to 100 cc., the color was a very dark brown with a slight purplish nuance, and the solution contained flocculated material. This experiment clearly indicated that fructose destroys the blue ninhydrin-amino acid compound when the latter has been formed, in addition to possible destruction of ninhydrin itself. This experiment also explains the formation and disappearance of the blue color in the test on the honey mentioned in the first paragraph.

In testing white sugars which have become "creepy," it often happens that a light brown color is obtained instead of the violet color of the ninhydrin-amino acid compound. One such sugar was found to contain 4.2 per cent invert sugar. In the test, since 1 gram of sugar was used, 42 mg. of invert sugar were present. With low concentrations of amino acids such as are normally encountered in white sugars, this quantity of invert sugar would be sufficient to destroy the violet color and produce a brown one.

Methods of detecting, and of possibly determining, this type of nitrogen compound in honeys are under investigation.

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RECEIVED July 6, 1931. Contribution 113, Carbohydrate Division, Bureau of Chemistry and Soils.

RESTORATION OF BRONZE AEGIS. The practice among early Egyptians of using various materials in effective combination is well illustrated by the inlaid bronze aegis recently acquired and restored by the Boston Museum of Fine Arts. While restoration of the object was under way, analyses of the metals were made by the Chemistry Department of the Massachusetts Institute of Technology. The main body of the object consists of a copper alloy, composed chiefly of copper and lead, while the inlays are of electrum, gilded silver, and true bronze. The piece dates from approximately the Twenty-second Dynasty,

or about 945 B. C., and some speculation has arisen as to why a copper and lead alloy was used instead of true bronze. Although Egypt had an abundance of copper from the earliest times, tin was not known in appreciable amounts until late and was then imported. The copper-lead compound may, therefore, have been used for reasons of economy. On the other hand, Dows Dunham, assistant curator in charge of Egyptian Art at the Boston Museum, suggests that this particular alloy may have been employed to enhance the contrast between the body and the inlays, which were all originally of a golden color.

Electrometric Titration of Boric Acid

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THE direct determination of boron in dilute aqueous solutions as described by Foote (2) calls for a highly sensitive method of titration. The Cavanagh (1) electrometric method has been successfully used for this titration. The electrometric method is rapid and accurate and is especially well adapted to measuring the small amounts of boron found in irrigation waters.

The observation made by Foote and utilized in the method here described is essentially the following: A dilute acid solution of mixed salts containing boron as boric acid is titrated to a neutral point near pH 7; the solution becomes acid upon the addition of mannitol and the quantity of alkali required to titrate the solution back to the same neutral point is an accurate measure of its boron content. By this procedure the pH at the initial and end point of the boron titration is the same.

Cavanagh makes "application to electrometric titration of the long-known principle of the Helmholtz cell or cell without liquid junction. A familiar example of this type of cell is that consisting of a hydrogen electrode and.... a silver chloride electrode in one and the same solution." The e. m. f. of this cell at the temperature T is:

$$E = E_0 + \frac{2RT}{F} \log_e C$$

where E_0 is a constant and C is the concentration of hydrochloric acid times its activity coefficient.

At a temperature of 16° C. the e. m. f. of a solution containing hydrogen and chloride ions is expressed by:

$$E = E_0 + 0.05735 \log_{10} (C_H \times C_{Cl})$$

where C_H and C_{Cl} are "corrected concentrations" or activities.

Using a silver chloride-quinhydrone cell and various concentrations of the two ions, Cavanagh obtained a mean value of 0.4740 for E_0 . At the end point of the titration, the equation may be written:

$$E = 0.4740 + 0.05735 \log_{10} (H) + 0.05735 \log_{10} (Cl)$$

With this value for E_0 , E vanishes in a solution with a pH of 7.62 and a chloride concentration (\times the activity coefficient) of 0.209 equivalent per liter. Likewise, in a solution with a pH of 7.3 and a chloride concentration (\times the activity coefficient) of 0.108 equivalent, E vanishes. At a lower pH, for instance, 5.62, E vanishes when the chloride concentration (\times the activity coefficient) equals 0.0022 equivalent per liter.

The fact that the pH at which E_0 vanishes can be predetermined by the adjustment of the chloride concentration makes it possible to adapt this electrometric titration to the Foote procedure for the titration of boric acid.

APPARATUS

The quinhydrone electrode is made from platinum wire 1 mm. in diameter and 6 cm. long. The wire is cleaned in hot sulfuric-chromic acid and "blanked" in an alcohol flame, as suggested by Cavanagh. It is sealed into a glass tube and external connection made by means of mercury. The quinhydrone, supplied by the Eastman Kodak Company, is used without further purification.

The silver chloride electrode is made from a piece of 1-

mm. silver wire 10 cm. long. This is half submerged and made the anode (a piece of platinum wire, the cathode) in a 0.1 N sodium chloride solution and a current of about 2 milliamperes passed for an hour. Cavanagh states that a number of these electrodes may be prepared at a time and stored for a week or more in the dark in distilled water. In use, the two electrodes are held parallel from binding posts and about 1 cm. apart.

The galvanometer is of the pointer type and sensitive to 0.25×10^{-6} amperes per division, with a shunt and tap key in the circuit. The latter is preferably located on the floor to be operated with the foot. A small mechanical stirrer completes the equipment.

PROCEDURE

Transfer 250 cc. of the solution to a 400-cc. beaker. This should not contain over 1 mg. of elemental boron. (Larger quantities of boron can be titrated, but a more concentrated standard alkali solution should be used, as the total volume used between the initial and final points should not be greater than about 5 cc.) Add to the sample sufficient sodium chloride solution (12.5 cc. of 2 N sodium chloride) to bring the chloride concentration to 0.1 N . The small amounts of chloride usually found in irrigation waters can be neglected as the absolute chloride concentration is not critical. However, the chloride concentration should be altered as little as possible between the initial and final points, hence the use of a small volume of titrating solution and adjusting the aliquots to its concentration. Add a few drops of bromothymol blue (phenol red or sofno red may be used) and acidify with 1 N sulfuric acid, adding about 0.5 cc. in excess. Boil 3 minutes to expel carbon dioxide. Cool and add carbon dioxide-free sodium hydroxide to approximate neutrality. Add sufficient quinhydrone to saturate the solution (approximately 0.2 gram). Introduce into the solution the two electrodes which are connected through the shunt and tap key to the galvanometer. Add carefully carbon dioxide-free sodium hydroxide until a null point is indicated on the galvanometer. The solution should be stirred for a short time to make certain that equilibrium has been reached. This is the initial point of the titration and should be at about pH 7.3 at 16° C. Add 10 grams of neutral mannitol. Boric acid in the presence of mannitol titrates as a reasonably strong monobasic acid. The acidity of the solution will therefore increase and in case the tap key is closed at this point, the galvanometer should be protected by the shunt. Add standard alkali until the null point is again reached. This is the end point of the titration. The standard alkali used for the titration is carbon dioxide-free 0.0231 N sodium hydroxide, of which 1 cc. is equivalent to 0.25 mg. of boron, or with a 250-cc. aliquot, to 1 part per million of boron in the original solution. The buret should be of such accuracy that the volume of alkali used may be estimated to 0.01 cc. From the gross volume a blank is deducted. This blank is determined by substituting distilled water for the sample and proceeding as indicated above. The sodium hydroxide is standardized by titrating known amounts of pure boric acid.

RESULTS

Pure boric acid was ground to a fine powder and dried to constant weight over calcium chloride. From this, a solution

of boric acid was prepared, containing 0.1077 mg. of elemental boron per cc. Aliquots of this solution were titrated by the above described method with the results shown in Table I.

TABLE I. TITRATION OF SOLUTION OF PURE BORIC ACID BY ELECTROMETRIC METHOD

BORIC ACID SOLN.	EQUIVALENT BORON	0.046 N SODIUM HYDROXIDE Total	Less blank	BORON PER CC. OF SODIUM HYDROXIDE
Cc.	Mg.	Cc.	Cc.	Mg.
0 (blank)	0	0.04	0.06 used as blank	
0 (blank)	0	0.07		
0 (blank)	0	0.08		
2.5	0.269	0.60	0.54	0.498
2.5	0.269	0.59	0.53	0.508
2.5	0.269	0.61	0.55	0.489
5.0	0.538	1.13	1.07	0.503
5.0	0.538	1.13	1.07	0.503
5.0	0.538	1.11	1.05	0.512
10.0	1.077	2.25	2.19	0.492
10.0	1.077	2.15	2.09	0.515
10.0	1.077	2.20	2.14	0.503

TABLE II. BORON DETERMINATIONS ON IRRIGATION WATERS BY ELECTROMETRIC-TITRATION METHOD

LAB. NO.	BORON, DUPLICATE DETNS.		BORON RECOVERED
	P. p. m.	P. p. m.	Mg.
4519	0.21	0.17	1.19
4522	0.02	0.04	1.23
4525	0.04	0.05	1.24
4528	0.10	0.05	1.23
4531	0.06	0.04	1.22
4534	0.13	0.13	1.19
4537	0.19	0.11	1.23
4540	0.10	0.17	1.22
4543	0.10	0.09	1.21
4546	1.16	1.19	1.25
4549	0.60	0.63	1.20
4552	0.22	0.15	1.23
4555	0.07	0.05	1.20
4558	0.11	0.09	1.20
4564	1.22	1.25	1.21
4567	0.35	0.29	1.15
4570	0.22	0.22	1.21
4573	0.64	0.65	1.24
Av.	0.31	0.30	1.214

The results of the boron determinations of a series of natural waters are reported in Table II. The figures represent duplicate determinations on separate aliquots. To a third aliquot of each sample 1.21 mg. of boron as boric acid were added. Column 4 shows the recovery of this added boron expressed in milligrams of boron.

The method here described has been used on 300 samples of irrigation water in comparison with the modified Chapin method (3) with satisfactory results. The boron content of such waters as determined by direct titration is consistently slightly higher than that obtained by the distillation method, but since it is known that by the latter method only 90 to 95 per cent of the boron is recovered, it is believed that the results by the direct-titration method are nearer the truth.

The direct-titration method may not be dependable for use with solutions containing appreciable quantities of phosphates, such as the nutrient solutions used in the plant cultures, or with solutions containing relatively high concentrations of silicates. It is recommended for use with irrigation and drainage waters in which the range of hydrogen-ion concentration is usually between pH 7 and 8, and in which the content of phosphates and silicates is low.

ACKNOWLEDGMENT

The author wishes to acknowledge his indebtedness to Francis Scofield, who first pointed out the possibilities of the Cavanagh procedure in the titration of boric acid, and also to Albert P. Vanselow and Frank M. Eaton for suggestions during the early part of this work.

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Determination of Boron in Waters

Method for Direct Titration of Boric Acid

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MOST procedures for the determination of boron necessitate the absence from the solution of all other substances titrating between a pH of about 5 and a pH of about 8.4. To eliminate these substances from a sample containing less than one part per million of boron without the loss of some boron or the addition of a varying amount with the reagents used has been found to be a troublesome and time-consuming process. In the past year a method has been developed and used for titrating boron in irrigation waters and water extracts of soils which overcomes this difficulty, and determinations made by it are rapid and capable of great accuracy. This method should be applicable to any aqueous solution of boron, although modification may be necessary in some instances.

Results by the direct method have been compared with results by the distillation method formerly used in this laboratory, and the new method found to be more reliable (1). Hundreds of determinations have been made on waters and soil extracts without encountering any trouble.

The principle of the determination is that with no mannitol present, boric acid is so weak that it is only partially neutralized at a pH of 7.6, but in the presence of sufficient man-

nitol it is completely neutralized at this pH. No other acids or bases encountered or tested are affected by mannitol, so that the boric acid can be accurately titrated by bringing the solution to a pH of 7.6, adding mannitol, and titrating back to the same pH. The alkali used for titrating is standardized against a known amount of boric acid in the same manner, so that the small amount neutralized up to pH 7.6 is taken care of in the standardization factor. The amount so neutralized is about 12 per cent of the total boric acid present. Since there is no pH change involved in the two end points, there is no interference from other substances in the solution. It has been found, however, that the solution must be practically free of carbon dioxide, or equilibrium is difficult to attain and low results are obtained. Curves illustrating the titration of boric acid are shown in Figure 1. The initial point for the direct titration is A, and the end point is B.

DETERMINATION OF pH

For the determination of pH, either colorimetric or electrometric apparatus may be used. The colorimetric method has been used for most of the determinations and found en-

tirely satisfactory where a practically water-white solution, not highly buffered at pH 7.6, is titrated.

The details of the procedure used for determining boron in water samples, using the colorimetric pH indicator, are as follows: Put 100 to 500 cc. of sample into a 250- or 500-cc.

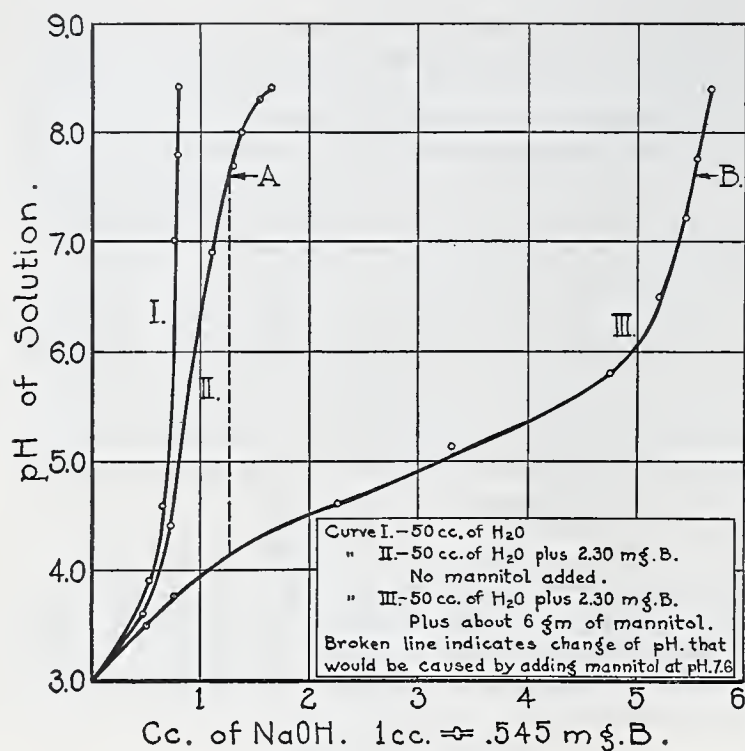


FIGURE 1. TITRATION OF BORIC ACID

wide-mouth Pyrex Erlenmeyer flask. Make distinctly acid to methyl red with hydrochloric acid, using only one drop of a 1 per cent solution of methyl red so that it will not interfere with the pH determination later. Boil gently 5 minutes with two or three stirrings to drive off carbon dioxide. Cool to room temperature. Add 5 drops of 0.4 per cent phenol red indicator for every 100 cc. of sample. This must be regulated so as to have the same color concentration as is used with the standard pH indicator. Stopper the flask with the stopper described below and adjust the pH to 7.6 with carbon dioxide-free, approximately 1.0 *N*, sodium hydroxide. Equilibrium is more quickly established if enough sodium hydroxide is added to give a pH of 8.0 to 8.4, the solution vigorously shaken for 10 or 15 seconds, and then adjusted to pH 7.6 with approximately 0.1 *N* hydrochloric acid and 0.015 *N* sodium hydroxide. Equilibrium can be assumed when there is no perceptible change of color with 15 or 20 seconds of vigorous shaking. One should not proceed until the pH is constant at 7.6 while shaking for this length of time. This is the initial point and the buret should be read. Add 3 grams of mannitol for every 100 cc. of solution, and immediately titrate back to 7.6 with standardized sodium hydroxide, taking care that exhaled carbon dioxide does not enter the flask. This is the end point of the titration and the pH should remain constant while shaking vigorously for 15 or 20 seconds as before. Read the buret. The sodium hydroxide used is 0.015 to 0.02 *N*. (1 cc. equivalent to 0.160 mg. of boron has been found satisfactory.) Standardize this with a known amount (1 to 5 mg.) of boric acid in 100 or 200 cc. of distilled water by the same procedure as the determination. It is convenient to use 10 cc. of a solution containing 0.7145 gram of boric acid in 500 cc. for standardization (1 cc. contains 0.25 mg. of boron). Subtract a blank titration, using the same amount of mannitol in distilled water, from all determinations.

In order to get the most accurate colorimetric results, it is necessary to match the color of a LaMotte ampul pH indicator. The solution cannot be poured through the air into

a test tube for comparison as the carbon dioxide absorbed might appreciably affect the results. To overcome this, place a test tube in the stopper of the flask so that it can be filled by inverting the flask. Then compare it with the standard tube against a white background. The arrangement used is shown in Figure 2. The rubber connection should be heavy enough so that the tube will not flop around while shaking. If two tubes are used side by side, the ampul standard is not absolutely necessary. One tube can be left filled and clamped after equilibrium is established, and the titration completed on the remainder of the solution by matching the second tube with this. The second tube is then filled and clamped, the first tube drained, and the titration completed on the remainder of the solution by matching the solution in the second tube. This procedure can be used for off-colored solutions, but it is not generally so satisfactory as the separate ampul indicator, as the clamp might allow some solution containing mannitol to pass and the color in the tube would then fade. Also, some rubber tubing affects the pH in a short time.

The initial and end point of the titration need not be at pH 7.6. With sufficient mannitol present, the neutralization is complete at pH 6.0. More mannitol is required the lower the pH of the end point. The standardization factor for a solution titrated at pH 6.0 is not the same as at pH 7.6, because less boric acid is neutralized before the mannitol is added. However, Figure 1 shows that the curve without mannitol and the curve with mannitol are almost parallel between pH 6.5 and 7.6. Thus the results are practically the same over this range without changing the factor for the alkali. This is true only when sufficient mannitol is present

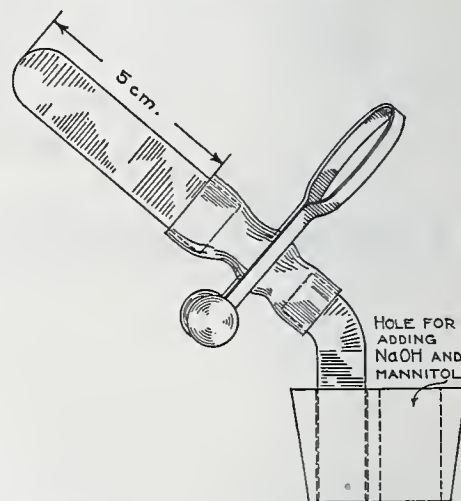


FIGURE 2. STOPPER USED IN COLORIMETRIC DETERMINATION

to cause all the boric acid to react at the lower pH. A pH higher than 7.6 can be used for the titration, but the amount of boric acid neutralized with no mannitol present is increased.

AMOUNT OF MANNITOL

The amount of mannitol needed varies with the volume of solution, the concentration of boron, and the pH used for the end point of the titration. In the usual procedure for titrating boric acid, successive additions of mannitol are made until the pH is not affected thereby. Such a procedure, with the large volume of sample titrated by the direct method, requires the use of a great deal of mannitol. If this reagent is not neutral, an appreciable error may be introduced by using varying amounts of it. The titration can be satisfactorily and advantageously performed by using a constant concentration of mannitol, but the concentration of boron must not exceed the maximum that the mannitol added will cause to react.

If pH 7.6 is used for the initial point, 3 grams of mannitol for each 100 cc. of solution are satisfactory for any concentration of boron up to 5 mg. per 100 cc. No ordinary water approaches this concentration. With more concentrated solutions of boron, more mannitol must be used, or the standardization factor is changed. All determinations and recoveries reported in this paper were titrated by using 2 grams of mannitol for every 100 cc. of solution. The alkali used was standardized with boric acid using the same concentration of mannitol. The addition of more mannitol would have increased all titration figures slightly. The amount of boron found would not be changed, however, as the decrease in

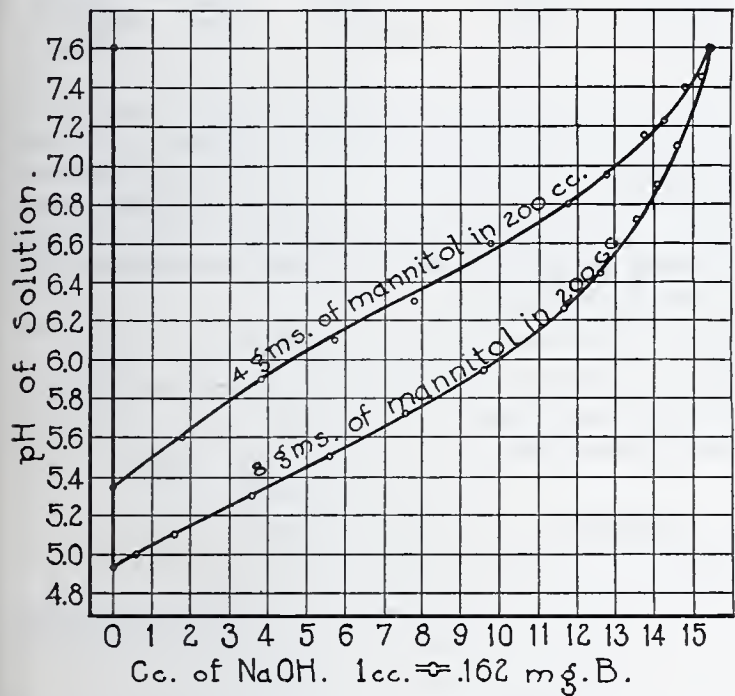


FIGURE 3. TITRATION OF 2.5 MG. OF BORIC ACID BY DIRECT METHOD WITH DIFFERENT CONCENTRATIONS OF MANNITOL

the standardization factor would offset the increase in the amount of alkali used. Figure 3 shows the path of the titration with 2.50 mg. of boron in 200 cc. in the presence of 4 and 8 grams (2 and 4 grams per 100 cc.) of mannitol. These curves show that increasing the concentration of mannitol 2 grams per 100 cc. does not greatly affect the amount of alkali used at pH 7.6. Therefore, the quantity of mannitol added need not be precisely measured. Three grams of mannitol for each 100 cc. are recommended for water samples, as the pH change near the end point is greater for a given amount of alkali than when 2 grams are used.

RESULTS OBTAINED USING METHOD

The direct-titration method of determining boron gives accurate results with small amounts of boron provided the solution is not too highly buffered. It has been used to determine the boron as impurity in such salts as calcium chloride, sodium carbonate, and sodium sulfate. If the solution is highly buffered, the cause of the buffering can be removed. In all cases where a precipitate is extracted, it should be tested for boron by dissolving or heating in dilute hydrochloric acid (pH 3 or below), and reprecipitating. The necessity for this is shown in the following determinations: Samples of 2500 cc. of water were evaporated to about 75 cc. in alkaline solution. The residue was filtered and washed with 100 cc. of hot water. The precipitate was dissolved by heating in 100 cc. of water and acid, made just alkaline to phenolphthalein with sodium hydroxide, filtered, and washed with 100 cc. of hot water. The redissolving and precipitating were repeated.

Boron determinations by direct titration were made on each filtrate. Results are shown in Table I.

TABLE I. BORON RETAINED BY PRECIPITATES

SAMPLE	TOTAL SOLIDS IN SOLN. IN ORIGINAL WATER P. p. m.	BORON RETAINED				BORON IN 500 CC. WITHOUT CONCENTRATING P. p. m.
		1st filtrate	2nd filtrate	3rd filtrate	Total	
		P. p. m.	P. p. m.	P. p. m.	P. p. m.	
433	1170	0.389	0.050	0.027	0.466	0.480
434	1028	0.341	0.060	0.016	0.417	0.425

There was evidently a small amount of boron retained after dissolving the precipitate twice. It has since been found that if sodium carbonate is used for the precipitation, less boron is retained than when sodium hydroxide is used.

Sodium carbonate was used in precipitating the alkali-insoluble material from acid-soil extracts which contained so much precipitate that neither colorimetric nor electrometric determinations of boron could be made. The procedure used was to heat 250 cc. of the 2-1 extract to boiling, add saturated sodium carbonate solution until just alkaline to phenolphthalein, and boil 5 minutes. Filter through a Büchner funnel with suction, and wash with 50 cc. of hot water. Redissolve the precipitate in 50 cc. of dilute acid, boil, make alkaline, filter, and wash as before. Repeat the redissolving and precipitating. All or an aliquot part of the combined filtrates can be used for the determination, as described for water samples. Determinations on the separate filtrates representing 150 grams of soil gave the results shown in Table II.

TABLE II. BORON RETAINED BY PRECIPITATES WITH ACID EXTRACTS OF SOIL MADE ALKALINE

SAMPLE	ALKALI USED TO PPT.	BORON RETAINED				By distillation method Mg.
		1st filtrate	2nd filtrate	3rd filtrate	Total	
		Mg.	Mg.	Mg.	Mg.	
LLL Rs.	NaOH	0.67	0.31	0.05	1.03	1.01
LLL Rs.	Na ₂ CO ₃	1.00	0.08	0.00	1.08	
LLL Rs.	Na ₂ CO ₃	0.87	0.20	0.00	1.07	
S-56	NaOH	1.20	0.33	0.04	1.57	1.45
V-S-8	Na ₂ CO ₃		1.10	0.05	1.15	

It is necessary to run a blank using approximately the same amount of reagents, as c. p. chemicals often contain appreciable amounts of boron.

Table III compares results of determinations on waters by the direct-titration method, using 10 grams of mannitol in 500 cc., with results by the distillation method.

TABLE III. COMPARISON OF DETERMINATIONS ON WATER SAMPLES BY DISTILLATION AND DIRECT-TITRATION METHODS

SAMPLE	DISTILLATION METHOD		DIRECT TITRATION (500 CC. OF SAMPLE)	
	Amt. of sample	Boron	Boron	
	Cc.	P. p. m.	P. p. m.	
433	2500	0.43	0.48	
434	2500	0.40	0.42	
435	2500	0.40	0.41	
436	2500	0.39	0.41	
437	2500	0.39	0.41	
438	2500	0.45	0.52	
439	1000	0.45	0.41	
440	1000	0.43	0.43	
441	1000	0.43	0.45	
442	1000	0.73	0.77	
443	1000	0.40	0.42	
444	1000	0.46	0.45	
445	1000	0.45	0.47	

As a rule the results of direct titration are slightly higher than the results of the distillation method. Some boron is lost by the distillation method, as it has been used here, especially when the sample is high in total solids. A recovery of 95 per cent is common when boron is added to distilled

water and determined by the distillation method. It is thought, therefore, that the results of the direct-titration method are more nearly correct.

Table IV shows results of duplicate boron determinations and results on different sized aliquots of the same water sample by the direct-titration method, using 2 grams of mannitol for each 100 cc. of sample.

TABLE IV. DUPLICATE DETERMINATIONS OF BORON IN WATER SAMPLES

(Comparison of results on different amounts of sample)						
SAMPLE	AMT. OF SAMPLE	BORON	AMT. OF SAMPLE	BORON	AMT. OF SAMPLE	BORON
	Cc.	P. p. m.	Cc.	P. p. m.	Cc.	P. p. m.
406	500	0.83	200	0.84	100	0.82
11	200	0.72	100	0.72
2731	500	0.78	500	0.78		
2831	500	0.75	500	0.74		
3931	500	1.05	500	1.07		
4231	500	3.06	250	3.10		
4731	500	3.34	250	3.30		
4831	500	3.05	500	3.06		
4931	500	1.21	225	1.17	225	1.16
5031	500	0.66	225	0.66		
5331	500	0.418	200	0.404	100	0.434
5431	500	0.409	200	0.411	100	0.419
9131 ^a	500	4.26	200	4.27	100	4.27

^a Pacific Ocean at Ventura, Calif.

The smaller samples are about as accurate as the larger ones. This is mainly due to the greater change of pH which a given amount of alkali will cause in a small sample as compared with a large sample. For small samples, a buret should be

used that is subdivided into 0.05 cc. and readings estimated to 0.01 cc.

Table V shows typical recoveries of boron when added to a water. All determinations were made on 500 cc. of sample using 10 grams of mannitol.

TABLE V. RECOVERIES OF BORON WHEN DETERMINED BY DIRECT-TITRATION METHOD

SAMPLE	Added Mg.	BORON Found Mg.	Recovered Mg.	ADDED BORON RECOVERED %
1831	0	0.455		
1831	0.500	0.960	0.505	101.0
433 A	0	0.279		
433 A	0.498	0.773	0.494	99.2
433 A	2.49	2.767	2.488	99.9
433 A	4.98	5.303	5.024	100.9
433 A	9.96	10.270	9.991	100.3

This report is not intended to be a complete study of the method for determining boron here described. The procedure has been developed primarily for determining boron in waters, and for waters in this region it is entirely satisfactory. Lack of time prevents further investigation into its possibilities; but no reason for failure on more concentrated aqueous solutions is known.

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Note on Micro-Dumas Method for Determination of Nitrogen

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IN ADAPTING the classical Dumas method for the determination of nitrogen in organic substances to a scale suitable for microanalysis, Pregl originally obtained too large volumes of gas in the micronitrometer (8). This error he showed was caused by the formation of carbon monoxide, "due to a permanent disturbance of the equilibrium between carbon dioxide on the one hand and carbon monoxide and oxygen on the other, caused by the red-hot copper spiral." Later Pregl (8) improved his method to overcome this error.

Experience in teaching Pregl's method at the University of Pittsburgh, inquiries which have come to this laboratory, and a search of the literature (1, 2, 4-7) all show that high results may still be obtained by this method.

Since by using the following very slight modification of Pregl's method practically theoretical figures have always been obtained, even by beginners, it seemed desirable to publish this note. Furthermore, the time required for the determination is appreciably shortened and no difficulty has been noted in getting "micro-bubbles" at the end of the analysis.

The directions given by Pregl (9) are followed exactly through the burning of the sample. The carbon dioxide is then turned on and the stopcock of the micronitrometer adjusted so that "one bubble rises per two seconds." At the end of 5 minutes (during which time the portion of the tube containing the sample is reheated), the flame of the long burner is turned down slightly (3). During the next 5 minutes the gas is slowly turned off, so that at the end of 10 minutes from the time of starting the carbon dioxide, the

gas for both burners is turned off completely. After 2 or 3 minutes the stopcock of the micronitrometer can be opened further and the bubbles allowed to rise as fast as possible. Here the only precaution necessary is to regulate the speed so that the bubbles do not go together and stop at the bottom of the graduated portion of the micronitrometer. In this manner various types of organic substances containing nitrogen have been analyzed successfully in this laboratory. The following are a few illustrations:

NITROGEN DETERMINATIONS

No.	SUB- STANCE	NITROGEN TEMP.	PRES- SURE	FORMULA OF SUBSTANCE	PERCENTAGE OF NITROGEN	
	Mg.	Cc.	° C.		Theory	Found
1	5.734	0.284	27	760	C ₈ H ₁₇ O ₃ N	5.49 5.44
2	5.244	0.261	28	759	C ₈ H ₁₇ O ₃ N	5.49 5.43
3	3.466	0.255	28	759	C ₁₄ H ₂₂ O ₅ N ₂	8.09 8.02
4	3.560	0.265	27	757	C ₁₄ H ₂₂ O ₅ N ₂	8.09 8.14

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Quantitative Spectrographic Studies of Co-Precipitation

I. Magnesium in Calcium Oxalate

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THE quantitative separation of calcium and magnesium has always been a time-consuming and rather uncertain procedure. The large number of papers pertaining to the separation of calcium as the oxalate, and the equally large number of opinions expressed are ample proof that the problem deserves further study.

Previously, investigators, in their estimations of contamination, have relied on loss of weight with a second precipitation or a gravimetric determination of the magnesium oxide in the precipitate. Because of the incomplete precipitation of calcium in many cases and the very small amounts involved, such methods have yielded a variety of conclusions.

With the hope of eliminating as many of the foregoing difficulties as possible, a study has been made by means of quantitative spectrographic methods. Gravimetric determinations have been made for each condition in order to determine the variation from the weight taken. Spectrographic determinations of the per cent of magnesium were made on a sample precipitated under identical conditions.

MATERIALS USED

Pure distilled water, showing no trace of magnesium spectrographically, was prepared by redistillation from alkaline potassium permanganate in an all-Pyrex still. All crystallizations and solutions were made from this water.

Constant-boiling hydrochloric acid was prepared by distillation of 6 *N* hydrochloric acid in an all-Pyrex still. The first and last portions were rejected.

Ammonium hydroxide, 6 *N*, was prepared by distillation of concentrated ammonium hydroxide into distilled water, cooled in ice. The ammonium hydroxide was prepared in liter quantities as used, and kept in paraffined bottles.

Pure ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, was prepared by crystallizing Riedel and de Haen's material three times from distilled water.

The stock solution of magnesium chloride was prepared by dissolving magnesium metal in constant-boiling hydrochloric acid. The solution gave no test for calcium. The magnesium chloride for spectrographic standards was prepared by crystallizing three times from redistilled water.

The hexahydrate of calcium chloride was prepared from Riedel and de Haen's $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, found to contain very small amounts of magnesium initially. The hexahydrate was recrystallized three times from redistilled water. Each crystallization was carefully prolonged for a period of 3 days. The final product showed less than 0.001 per cent magnesium by spectrographic analysis.

Asbestos was prepared by washing with dilute hydrochloric acid and ammonium hydroxide, and finally with water.

QUANTITATIVE spectrographic analysis is reliable and rapid in such cases where its use is justified. The method is here shown to be applicable throughout a range of 1 to 0.001 per cent magnesium and may, by further refinements, be extended to even lower concentrations.

It is found that magnesium contamination is dependent primarily upon the time of digestion after the solution is alkaline, and somewhat upon the time of precipitation and the amount of ammonium oxalate present, but is practically independent of the ammonium chloride content. The complete precipitation of calcium is dependent upon the presence of sufficient ammonium oxalate for both calcium and magnesium.

Both long-fiber and micro asbestos were used in equal quantities. The long fibers were separated and sorted by hand. This asbestos showed no loss on several ignitions, with or without intermediate washings.

SOLUTIONS. The stock solution of calcium chloride was prepared by weighing such a quantity of the liquid $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ as would give 0.40 gram of calcium oxide per 50 cc. This amount was found convenient to handle.

The solutions used in checking the method of analysis were prepared from the spectrographically pure $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. The

method of drying was the one used by Richards in the determination of the atomic weight of calcium (5). The decomposition of the chloride was found to be negligible. Two grams of the salt were found to require only 0.12 cc. of 0.1 *N* hydrochloric acid for neutralization. The anhydrous calcium chloride prepared in this manner was made by weight to a known concentration similar to that used in the regular analyses.

The spectrographic standards were prepared by weight from the same $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. The solution was then checked gravimetrically. From the solution of known concentration, a range of standards was prepared from 0.0001 to 1.0 per cent magnesium by introduction of measured volumes of a dilute solution of magnesium chloride. Each solution was of the same calcium and hydrochloric acid content as those prepared from the precipitates.

The precipitates for spectrographic analyses were obtained from a third sample made simultaneously with the two gravimetric determinations. The precipitate was caught in a small Hirsch funnel, using a filter paper. This method proved quite satisfactory, and at the same time eliminated possibility of contamination from asbestos, which might have resulted from the use of the gravimetric precipitates. The calcium oxalate thus obtained was ignited to calcium oxide under the same conditions as the others, using a platinum crucible. Solutions were obtained by dissolving 0.35 gram of precipitate in 4 cc. of constant-boiling hydrochloric acid.

APPARATUS. A mechanical stirrer was used for all precipitation. The stirring was accomplished at a slow rate, using a large S-shaped stirrer. A drilled cover for the beaker prevented entrance of dust particles. A short funnel, fed from a separatory funnel, delivered the precipitating reagent directly to the liquid in the beaker.

Pyrex glassware was used throughout. Several attempts to use quartz beakers, bottles, and stills gave serious magnesium contamination, apparently from a scale which came from the surface of the quartz.

Digestion was carried out on an electrically heated hot plate designed to maintain a temperature of 90° C.

Precipitates were ignited in an electric muffle made by the Barkmeyer Electric Laboratories. This furnace was capable of maintaining temperatures as high as 1300° C. and was found to be an invaluable means of ignition.

Platinum Gooch crucibles were used for filtration and ignition. No plates were used in making the matte. Three separate layers of asbestos were added, carefully packing each with a stirring rod. A fourth was then added and deposited evenly by settling. The crucible was dried for an hour at 110° C. and then ignited.

Desiccators filled with fresh anhydrous and potassium hydroxide were used throughout the work. Calcium chloride gave values of the order of 2 mg. too high.

was quite turbid (100 drops). The precipitate was then digested. If the precipitation was to be completed in one step, the total amount of ammonium hydroxide was added, omitting the intermediate digestion after 100 drops. Final or complete precipitation was made with constant stirring within a prescribed length of time, as determined by a calibrated tip for the separatory funnel containing the precipitating reagent. Alkalinity was determined by the use of a few drops of phenolphthalein. Precipitates were washed twice by decantation, using a hot dilute solution of ammonium oxalate and ammonium hydroxide. After transfer to the filter, the calcium oxalate was washed free from chlorides. All precipitates were placed in the cool furnace, heated to

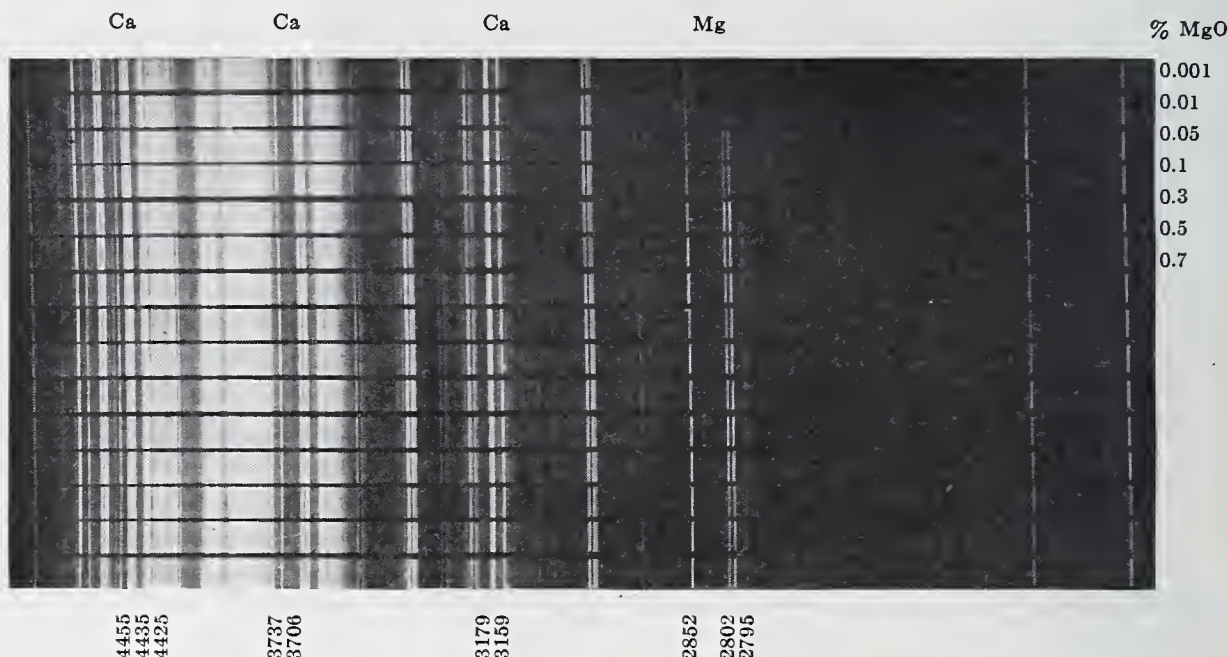


FIGURE 1. DETERMINATION BY SPECTROGRAPHIC METHOD

A Hilger E2 quartz spectrograph was used, giving a dispersion of 83 Å. per cm. at 2500, and 285 Å. per cm. at 4000.

The arc was operated on 110 volts d. c. Electrodes were of Acheson graphite, 2 inches (5.08 cm.) long, $\frac{5}{16}$ inch (0.79 cm.) in diameter, vertically opposed. The electrodes were held in position by screwing them into an aluminum disk, which also served to cool them to some extent.

The electrodes were found to contain relatively minute traces of magnesium, as purchased. The upper electrode, the negative pole, was cut in the form of a very blunt chisel, whose wedge-shaped end was set normal to the axis of the collimating lens of the spectrograph. The lower electrode, the positive pole, was drilled to a depth of 1 cm., using a $\frac{1}{8}$ -inch drill. The length of the arc was 3 mm. Each drilled electrode was burned in the arc 30 to 60 seconds to obtain a uniform, high porosity.

The plates used were Eastman 33, which were found to give very clear photographs in the region of investigation.

GENERAL METHODS OF ANALYSIS

Portions of calcium chloride solution to be used for analysis were weighed into 600-cc. beakers. To this amount sufficient hydrochloric acid was added to prevent the formation of a precipitate on addition of the ammonium oxalate. Magnesium ion in a 50-cc. volume was next added, if contamination was to be observed. The solution was then diluted with water to give a volume of 200 cc. and heated to first signs of boiling. The ammonium oxalate was then added in a 50-cc. portion. If two digestions were to be made, 3 N ammonium hydroxide was then added drop by drop until the solution

1075° C. (approximately 0.5 hour), and maintained at this temperature for 1 hour. More specific details accompany the experimental data.

Creeping was prevented by keeping the side of the beaker above the surface of the solution dry, save for the water which condensed, and by forming all precipitates within the solution rather than along the sides. It was for this purpose that hydrochloric acid was used to prevent a precipitate forming on addition of ammonium oxalate, and that a short funnel dropped the precipitating reagent directly into the solution.

For spectrographic determination, electrodes and solutions were prepared as previously described. Six drops of the solution to be analyzed, or of the standard, were placed in each electrode. The electrodes so prepared were dried in an oven at 110° C. for at least 6 hours. When not completely dry the arc does not burn well.

For the photography, the arc was set at the proper position as determined by the condensing lens and the spectrograph. The condensing lens should be mounted on a support clamped directly to the spectrograph. On the same support should be mounted a pointer showing the exact position of the arc. The arc was struck by shorting the poles with a carbon rod, the shutter on the slit being open so that the exposure began at once. After each 30 seconds the rheostat was adjusted to maintain a current of 10 amperes. Each exposure was timed at exactly 1.5 minutes. During the entire time, the arc was adjusted as a unit in a line normal to the axis of the collimating lens, so that the image fell directly on the slit. No effort was made to adjust the individual electrodes during the exposure. Nineteen photographs were taken on each plate. Final analysis of the plate was made visually by

light reflected from a white sheet of paper (Figure 1). Although this method was none too accurate, it was felt that visual estimation of intensities gave values as reliable as the method seemed to warrant. No claim is made that determinations are accurate beyond one significant figure.

The spectrographic method as described is essentially that given by Nitchie (4). Comparison with standards was made by photographing a series covering the expected range of precipitates, at the top of the plate, followed by the spectra for analysis.

This method was found to be as reliable as that of photographing the unknown between several standards.

Fortunately, the per cent of magnesium oxide in the precipitates was within the range which allowed the use of the five lines of wave lengths 2783, 2781, 2780, 2778, 2777 Å., where they were very weak. Comparison is much easier under such conditions.

EXPERIMENTAL RESULTS

Attention was first directed to possibilities of precipitation of magnesium oxalate. A few brief experiments were made to determine some characteristics. In each case 0.26 gram of magnesium ion, 1 gram of ammonium oxalate and ammonium hydroxide to alkalinity were used. The total volume was 225 cc. The results follow:

I. AT ROOM TEMPERATURE; DIGEST, NO STIRRING	
Hrs.	TURBIDITY
0	None
3	None
20	None
II. AT 100° C.; DIGEST, NO STIRRING	
0	None
3	None
20	Turbid
44	Very turbid
III. AT 100° C.; DIGEST	
0	None; stirred
2	None; stirred
2.5	Slightly turbid
3	Very turbid

Judging from these experiments and those of Fischer (2), the determinations were started with a variation in the time of digestion.

TABLE I. EFFECT OF VARIATION IN TIME OF DIGESTION ON CALCIUM OXALATE PRECIPITATE

(One digestion; wt. taken, 0.3963 gram of CaO)

TIME OF DIGESTION Min.	WT. WITH No Mg Gram	Mg EQUIVALENT TO Ca Gram	GAIN OVER WT. TAKEN %	WT. WITH No Mg %	MgO IN PPT. %
(1) 1.2 g. (NH ₄) ₂ C ₂ O ₄ ·H ₂ O, 12 cc. HCl (6 N), ppt. in 3 min.					
15	0.3957	0.3972			
	0.3961	0.3976			
30	0.3958	0.3960	0.27	0.4	0.8
	0.3961	0.3963	-0.02	0.05	0.8
60	0.3962	0.3951			
	0.3964	0.3963	-0.12	-0.12	0.4
		0.3954			
		0.3962			
(2) 2.4 g. (NH ₄) ₂ C ₂ O ₄ ·H ₂ O, 12 cc. HCl (6 N), ppt. in 7 min.					
15	0.3961	0.3964	0.1	0.1	0.1
	0.3964	0.3971			
30	0.3961	0.3964	-0.02	0.1	0.3
	0.3963	0.3969			
60	0.3957	0.3996	0.6	0.7	1.0
	0.3961	0.3978			

One and two-tenths grams of ammonium oxalate gave an excess of approximately 0.2 gram. Twelve cubic centimeters of hydrochloric acid (6 N) were required to keep the precipitate in solution. The per cent of magnesium oxide in the last column was determined by means of the spectrograph. This value should be equal to the per cent gain over the weight taken, if the calcium is completely precipitated. If such is not the case, the method is not suitable for a double precipitation. The values in the last three columns must approach zero if the method is suitable for a single precipitation.

Part 1 of Table I shows considerable magnesium oxide contamination. It is also evident that the calcium is not completely precipitated. A few determinations made with a magnesium-ion concentration one and a half times that of calcium did not increase the magnesium oxide contamination but further prevented precipitation of calcium. Part 2 shows that a digestion over 15 minutes is unsatisfactory. However, twice the required amount of ammonium oxalate is seen to remedy the incomplete precipitation of calcium. In this case, a magnesium-ion concentration one and a half times that of calcium made no appreciable difference. Table I is in keeping with Blasdale's suggestion that the oxalate ion is removed by formation of the little-ionized magnesium oxalate (1).

In the experiments tried so far, the precipitates were exceedingly fine-grained, and did not settle well. The next series (Table II) represents an attempt to form seed crystals by digestion in an acid solution, and subsequent formation of precipitates on these same crystals.

TABLE II. EFFECT OF VARIATION IN TIME OF FIRST DIGESTION ON CALCIUM OXALATE PRECIPITATE

(Two digestions; wt. taken, 0.3963 gram of CaO)

TIME OF DIGESTION 1st Hours	2nd Hour	WT. WITH No Mg Gram	Mg EQUIVALENT TO Ca Gram	GAIN OVER WT. TAKEN %	GAIN OVER WT. WITH No Mg %	MgO IN PPT. %
(1) 1.2 g. (NH ₄) ₂ C ₂ O ₄ ·H ₂ O, 12 cc. HCl (6 N), ppt. in 3 min.						
2.5	0.25	0.3963	0.3968	0.05	0.02	0.3
		0.3966	0.3962			
1.5	0.25	0.3959	0.3967	0.04	0.12	0.3
		0.3961	0.3956			
			0.3965			
			0.3965			
0.5	0.25	0.3954	0.3961	0.0	0.22	0.07
		0.3953	0.3965			
0	0.25	0.3957	0.3972	0.27	0.4	0.8
		0.3961	0.3976			
(2) 1.2 g. (NH ₄) ₂ C ₂ O ₄ ·H ₂ O, 12 cc. HCl (6 N), ppt. in 7 min.						
1.5	0.25	0.3960	0.3962	-0.04	0.0	0.1
		0.3963	0.3960			
0.5	0.25	0.3957	0.3963	0.05	0.05	0.2
		0.3961	0.3959			
0	0.25	0.3958	0.3961	0.02	0.05	0.3
		0.3963	0.3963			
(3) 2.4 g. (NH ₄) ₂ C ₂ O ₄ ·H ₂ O, 12 cc. HCl (6 N), ppt. in 7 min.						
1.5	0.25	0.3960	0.3960	-0.02	-0.02	0.07
		0.3963	0.3962			
		0.3966	0.3962			
		0.3963				
0.5	0.25	0.3957	0.3961	0.02	0.12	0.2
		0.3960	0.3967			
			0.3961			
			0.3967			
0	0.25	0.3961	0.3964	0.1	0.1	0.1
		0.3964	0.3971			

TABLE III. EFFECT OF VARIATION IN TIME OF SECOND DIGESTION ON CALCIUM OXALATE PRECIPITATES

(Two digestions; wt. taken, 0.3963 gram of CaO)

1.2 g. (NH₄)₂C₂O₄·H₂O, 12 cc. HCl, ppt. in 3 min.

TIME OF DIGESTION 1st Hours	2nd Hour	WT. WITH No Mg Gram	Mg EQUIVALENT TO Ca Gram	GAIN OVER WT. TAKEN %	GAIN OVER WT. WITH No Mg %	MgO IN PPT. %
1.5	0.25	0.3959	0.3967	0.05	0.12	0.3
		0.3961	0.3965			
1.5	0.5	0.3956	0.3958	-0.1	0.0	0.3
		0.3961	0.3960			
1.5	1	0.3963	0.3965	0.04	0.02	0.5
		0.3965	0.3965			

The formation of seed crystals proved to be useless in Part 1 of Table II, probably because of too rapid precipitation. Parts 2 and 3, however, produced precipitates which settled out very quickly where the first digestion was 1.5 hours. Microscopic examination disclosed aggregates of crystals.

Interestingly enough, decreasing the time of the first digestion increases the magnesium oxide contamination in every case, except in Part 3. The addition of double the amount of ammonium oxalate again brings the results into closer accord.

The increase in time of precipitation appears as an intermediate step between Parts 1 and 3.

A variation in the time of the second digestion (Table III) gave results somewhat analogous to Part 1 of Table II. Here again the data point to the fact that a digestion of more than 15 minutes after the filtrate has been made alkaline gives progressively poorer results.

Another possibility for variation was the ammonium chloride content. The variation was produced by addition of hydrochloric acid.

Contrary to the usually accepted ideas, the amount of ammonium chloride has no appreciable effect. If anything, it is undesirable, as in Part 4 of Table IV.

TABLE IV. EFFECT OF AMMONIUM CHLORIDE ON CALCIUM OXALATE PRECIPITATES

(Wt. taken, 0.3963 gram of CaO; Parts 1, 3, and 4, two digestions; Part 1, one digestion)

TIME OF DIGESTION	NH ₄ Cl	WT. WITH Mg	GAIN OVER	MgO IN
Hours	Grams	EQUIVALENT TO Ca	WT. TAKEN	PPT.
		Gram	%	%
1st 2nd	(1)	2.4 g. (NH ₄) ₂ C ₂ O ₄ ·H ₂ O, ppt. in 7 min.		
1.5 0.25	4	0.3963 0.3960	-0.02	0.07
	8	0.3961 0.3967	0.2	0.1
1	(2)	1.2 g. (NH ₄) ₂ C ₂ O ₄ ·H ₂ O, ppt. in 3 min.		
	4	0.3962 0.3964	-0.12	0.4
	8	0.3965 0.3961	0.0	0.5
1.5 0.25	(3)	1.2 g. (NH ₄) ₂ C ₂ O ₄ ·H ₂ O, ppt. in 7 min.		
	4	0.3960 0.3963	-0.04	0.1
	8	0.3949 0.3948	-0.35	0.1
1.5 0.25	(4)	1.2 g. (NH ₄) ₂ C ₂ O ₄ ·H ₂ O, ppt. in 3 min.		
	4	0.3959 0.3961	0.07	0.2
	8	0.3944 0.3951	-0.4	0.7

A further possibility presented itself in the addition of ammonium oxalate to the alkaline solution rather than the ammonium hydroxide to the solution containing the oxalate.

Although the reverse method, whose results are given in Table V, is unsatisfactory for analysis, it is interesting to note that the contamination is practically constant. Such results are to be expected where the solutions in which the precipitates are formed are very similar.

With the completion of the part of the work in which no magnesium was used, the method using two digestions of 1.5 and 0.25 hour, shown in Part 3, Table II, was chosen as the most convenient method, giving the highest value and the most granular precipitate. It was therefore used in the analysis of the known solution of calcium chloride prepared by Richards' method of drying. The results shown in Table VI prove the method, and it was subsequently used to standardize the stock solution.

TABLE V. EFFECT OF REVERSE METHODS ON CALCIUM OXALATE PRECIPITATES

(Wt. taken, 0.3963 gram of CaO; one digestion except in last part)

TIME OF DIGESTION	WT. WITH Mg	GAIN OVER	MgO IN
Hours	EQUIVALENT TO Ca	WT. TAKEN	PPT.
	Gram	%	%
0.25	1.2 g. (NH ₄) ₂ C ₂ O ₄ ·H ₂ O, 12 cc. HCl (6 N), ppt. 3 min.		
	0.3960 0.3964	0.0	0.5
1	1.2 g. (NH ₄) ₂ C ₂ O ₄ ·H ₂ O, 12 cc. HCl (6 N), ppt. 3 min.		
	0.3961 0.3967	0.2	0.6
0.25	1.2 g. (NH ₄) ₂ C ₂ O ₄ ·H ₂ O, 12 cc. HCl (6 N), ppt. 7 min.		
	0.3946 0.3953	-0.35	0.5
0.25	2.4 g. (NH ₄) ₂ C ₂ O ₄ ·H ₂ O, 12 cc. HCl (6 N), ppt. 7 min.		
	0.3984 0.3999	0.6	0.6
1st 2nd	2.4 g. (NH ₄) ₂ C ₂ O ₄ ·H ₂ O, 12 cc. HCl (6 N), ppt. 7 min.		
1.5 0.25	0.3972 0.3977	0.27	0.5

TABLE VI. TEST OF METHOD BY STANDARD CALCIUM CHLORIDE SOLUTION

	EXPERIMENTAL WT.	CALCD. WT.
	Gram	Gram
I	0.3545 0.3547	0.3546
II	0.3927 0.3930	0.3930

Finally, regarding the data as a whole, there are only two methods satisfactory for either single or double precipitation. These are the methods tested by the known solutions (Table II, Part 3), and the 0.25-hour digestion in Table I, Part 2. In either case, the error of a single precipitation is only 0.0004 gram for a magnesium content as high as one and a half times the equivalent of calcium.

TABLE VII. TEST BY SINGLE AND DOUBLE PRECIPITATION OF CALCIUM OXALATE

TIME OF DIGESTION	WT. TAKEN	1 PPTN.	2 PPTNS.	MgO BY DIFF.
Hours	Gram	Gram	Gram	IN WT. %
0.25	2.4 g. (NH ₄) ₂ C ₂ O ₄ ·H ₂ O, 12 cc. HCl (6 N), ppt. 7 min.			
	0.3729	0.3734 0.3735	0.3727 0.3728	1.8
1st 2nd	2.4 g. (NH ₄) ₂ C ₂ O ₄ ·H ₂ O, 12 cc. HCl (6 N), ppt. 7 min.			
1.5 0.25	0.3930	0.3928 0.3930	0.3927 0.3931	0.0

As a further check, values, given in Table VII, were obtained using both single and double precipitations, again using a magnesium concentration equivalent to that of calcium. The only essential difference between the two is the 1.5-hour digestion in acid solution preceding final precipitation. The shorter method does not give as granular a precipitate as the other, and is therefore less easily filtered.

The accepted method is as follows:

Start with a sample which will give about 0.35 gram of calcium oxide. Adjust the volume of solution to 200 cc., and heat to boiling. Add twice the necessary amount of ammonium oxalate in a 50-cc. volume, preventing precipitation by addition of hydrochloric acid. Then add ammonium hydroxide (3 N), drop by drop, until the solution is quite turbid. About 100 drops are necessary. Digest the precipitate for 1.5 hours at 90° C. Then complete the precipitation during a period of 6 to 8 minutes with constant stirring. Digest for 0.25 hour longer, then filter and wash at once. Ignite the precipitates in platinum to a temperature of 850° C. or more. Cool in a desiccator containing anhydrous P₂O₅ and potassium hydroxide.

Efforts to discover the way in which magnesium contaminates the precipitates met with little success. By means of a cataphoresis cell, all the particles were found to be charged negatively before washing, and possessed no charges after washing. This points to occlusion of Cl⁻ or C₂O₄²⁻ rather than Mg⁺⁺.

The crystals were too small to be of value under the polarizing microscope. Those in which magnesium occurred were in the order of fifteen times larger, however, and appeared to be monoclinic in some cases. Groth (3) states that crystals formed from a warm concentrated solution are the monoclinic calcium oxalate. Magnesium oxalate likewise appeared to be monoclinic. The data, however, are so very doubtful that one can only suggest that the magnesium is isomorphous with calcium, and that the larger crystals are due to the crystal habit of Ca, Mg(C₂O₄)₂ × H₂O.

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Shellac

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DETERMINATION OF COLD INSOLUBLE, WAX, AND ASH

THE term "insoluble," when used in connection with shellac, is understood to mean that material which is insoluble in ethyl alcohol, consisting usually of sand, insect remains, and arsenious sulfide, exclusive of wax. Occasionally there may be present insoluble (polymerized) shellac resin, insoluble in cold but partially soluble in boiling alcohol. If so, determination by the hot-alcohol method (1) would therefore yield inaccurate results.

The official cold-alcohol method (11), which is recommended for the determination of polymerized shellac, specifies the use of 124-mesh silk as the filtering medium, and the results obtained are always lower than actuality because of the passage of small particles of insoluble matter through the +0.120-mm. openings.

Shellac wax is also insoluble in cold alcohol and soluble in boiling alcohol, chloroform, or carbon tetrachloride. As it is considered to be a normal constituent of shellac up to 5.5 per cent, it is determined and reported separately (2).

However, by retaining cold alcohol as the solvent, filtering through paper or alundum crucibles, and extracting the wax with hot chloroform, accurate determinations of the insoluble matter and polymerized resin can readily be made.

METHOD. The sample of shellac should be ground to pass 100 per cent through a No. 30 sieve, and thoroughly mixed to insure uniformity. Place 5 grams in a 200-cc. lipped beaker, and add 100 cc. of 95 per cent alcohol (No. 1 or 30 specially denatured). Stir frequently for 2 hours to dissolve all the soluble matter. Next stand the beaker in an ice-water bath, at 5° C., for 2 hours without stirring. A low temperature facilitates settling and filtration.

TABLE I. INSOLUBLES, WAX, AND ASH, IN SHELLACS

	ORANGE TN PURE 1	ORANGE 2	TN USSA 3	BLEACHED 4	DRY 5 ^a	BLEACHED DRY REFINED 6
	%	%	%	%	%	%
Cold insoluble, new method	3.77	3.06	2.48	0.34	2.59	0.68
Wax	4.18	4.00	3.98	4.80	4.20	0.20
Ash	0.75	0.64	0.93	0.10	0.25	0.05
Hot insoluble	3.65	3.05	2.82	0.38	0.55	0.37
Cold insoluble, official method	1.37	1.40	1.30	0.05	1.65	0.00
Iodine value	17.20	22.90	20.70	7.70	7.60	6.30

^a Contained polymerized shellac.

Meanwhile, ignite an RA-98 porous alundum thimble at low red heat for about 15 minutes, cool, and weigh.

Place the thimble in a carbon filter-tube, 32 mm. in diameter and 70 mm. in depth, whose stem passes through a rubber stopper in the neck of a 500-cc. filter flask.

Decant the shellac solution into the thimble, washing the insoluble from the beaker with about 100 cc. of cold alcohol and using a policeman. Apply a moderate vacuum, if necessary.

Next extract the thimble containing the insoluble and wax with hot chloroform in a Soxhlet extractor for 1 hour to extract all of the wax. Dry the thimble at 105° C. for 2 hours or more to constant weight, and the percentage of cold alcohol-insoluble matter can be calculated.

The amount of ash can be determined by igniting the thimble until the carbon is destroyed, cooling, and weighing.

After distilling off most of the chloroform from the wax extract in a weighed flask, the wax can be dried at 105° C. to constant weight.

Some typical comparative results by this method are shown in Table I.

SPECIFIC GRAVITY

Oberdoerffer (10) gives a specific gravity value of 1.205 for "pure" shellac. Coffignier (5) found values of 1.009, 1.036, and less than 1 at 16° C., for sticklac, pale orange, and bleached shellac, respectively. Hooper (7) reports 1.139 for lac resin. Langmuir (9), Olsen (12), Thorpe (13), and Hodgman and Lange (6) publish values of 1.08 to 1.13 for shellac. Hurst (8) states that lac has a specific gravity of 1.113 to 1.214, the darker varieties being the heavier. Wolff (14) found values of 1.035 to 1.14 at 15° C. for shellac.

The method employed is not stated by any of the authors. In only two instances is the temperature reported and in only one instance is the grade of shellac reported on clearly stated. The values reported show an evident lack of agreement.

Bradley (4) found values of 1.152 for orange superfine, and 1.110 for bleached dry shellac at 20° C., by displacement of water. As shellac adsorbs water to some extent and swells, determination in water may influence the accuracy of the results.

As previous experiments had shown that shellac was insoluble in and unaffected by kerosene, the specific gravities of three common varieties of shellac were determined in this liquid.

A convenient method which specifies the use of kerosene as the displacement medium is Standard Methods of Test for Specific Gravity of Pigments, A. S. T. M., D 153-27, Method A, and after proper preparation of the shellac this method (3) was followed.

The three varieties selected were TN pure orange, containing 2.75 per cent insoluble, dry bleached 0.6 per cent insoluble, and dry bleached refined 0.4 per cent insoluble.

Each sample was ground to pass 100 per cent through a No. 120 sieve (0.125-mm. openings), and dried at 42° C., in an air-bath for 18 hours to eliminate adsorbed moisture and gases. It was then re-sieved, and from 0.300 to 0.600 gram was filled into a weighed 25-cc. pycnometer in the air-bath. After weighing the pycnometer and shellac at room temperature, the shellac was completely covered with kerosene. Thereafter the method was followed in detail. The results are shown in Table II.

TABLE II. SPECIFIC GRAVITY OF SHELLACS

(At 15.5°/15.5° C.; moisture-free)

ORANGE TN PURE	BLEACHED DRY	BLEACHED DRY REFINED
1.196	1.198	1.214
1.199	1.194	1.226
1.212	1.199	1.223
1.216	1.193	1.207
1.212	1.190	...
...	1.187	...
...	1.211	...
Av. 1.207	1.196	1.217

As shellac wax is soluble in kerosene, the specific gravity of a sample of known purity, unbleached, was determined in 95 per cent alcohol instead, by the same method.

Moisture-free, at 15.5°/15.5° C., the specific gravity of shellac wax was found to average 1.028.

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the more commonly employed method (3) for determining this number consists in refluxing with 0.5 *N* alcoholic potassium hydroxide for a half hour, and back titrating the excess potassium hydroxide, after cooling, with 0.5 *N* aqueous hydrochloric acid, using phenolphthalein as an outside indicator.

Many of the early workers endeavored to devise special methods for the saponification of shellac. Mills (11), for example, dissolved 1 gram in 25 cc. of alcoholic 0.5 *N* potassium hydroxide, and saponified for 18 hours in a closed flask. He obtained a number of values for varied grades of shellac, obtaining as high as 230 for an orange. Williams (15), on the other hand, used the usual method, refluxing for a half hour, and obtained lower values varying from 194 to 212. E. Dieterich (3) used the same method as Williams but concentrated the mixture until all the alcohol was expelled and then took up the residue with water and ethyl alcohol before titrating with acid.

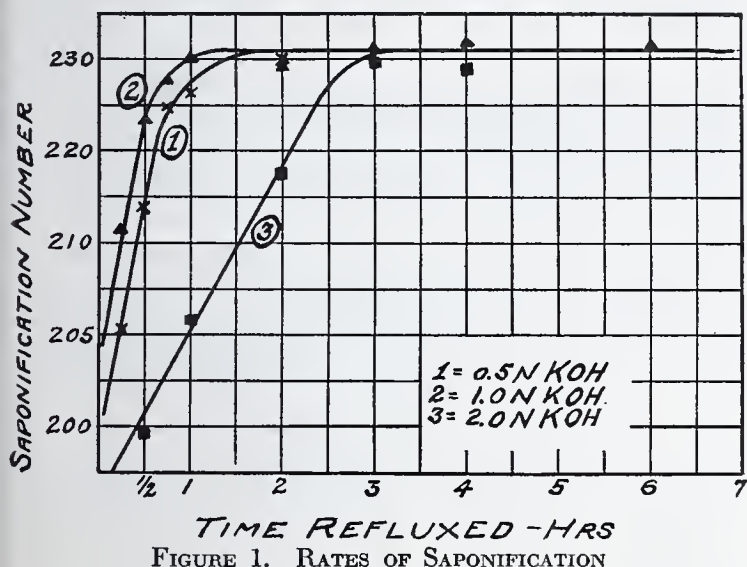


FIGURE 1. RATES OF SAPONIFICATION

K. Dieterich (3) used two methods. The first was a cold saponification, where the resin was allowed to react with a benzene-alcoholic potash solution for 24 hours. The other method depends on a fractional saponification, where the resin is subjected to the action of alcoholic alkali for 24 hours, and then of aqueous alkali for 24 hours more. He reports that the latter method gave higher results than the former. Singh (14) investigated orange shellacs in particular, using the common method employed by Williams. His values check well, 210 to 203, as compared with 206 obtained by Williams.

Nagel and Körchen (12) state that even as low concentration as 0.1 *N* potassium hydroxide will effect saponification, but only on prolonged heating. With 0.5 *N* alcoholic potassium hydroxide they obtained numbers ranging from 190 to 225, and for garnet lacs values as low as 175. They stress the fact that variations in the values for different samples are not due to the method, but to differences in the material. They do not state any specific time for refluxing and claim that the use of aqueous acid for titrating gives a less accurate end point than alcoholic hydrochloric acid.

SPEED OF SAPONIFICATION REACTION

From previous experience in these laboratories, it seemed advisable to limit this investigation to a study of alcoholic potassium hydroxide solutions, since preliminary experiments had indicated that this solvent gave the most rapid and complete saponification. The speed of reaction was determined for 0.5 *N*, 1.0 *N*, and 2.0 *N* alkali.

Superfine orange shellac was used for these experiments. The material was ground to pass completely 30 mesh, and a

200-gram sample was thoroughly rolled to secure a homogeneous mixture. It is essential that the sample be most carefully prepared in this manner. Smaller variations in sampling will materially affect the saponification number. Representative portions of 5 grams were accurately weighed from this sample and treated with 50 cc. of alkali in every case. Saponification numbers were obtained for 0.25 to 6 hours' refluxing. During the saponification the solution was protected from any possible error from carbon dioxide of the air by closing the condenser with Kipp generator bulbs. After refluxing, the excess alkali was titrated with standard aqueous hydrochloric acid, using thymol blue as the outside indicator. Since alkaline shellac solutions are dark purple in color, this indicator, which is a deep blue at pH 9.6 and yellow at pH 8.0, was found to give an end point which could be more easily judged than phenolphthalein. Blanks of 50 cc. alkali were run in all cases. Three samples were run for check results.

The results are summarized in Tables I to III and shown graphically in Figure 1. It can be seen from this graph that when sufficient time has been allowed for complete reaction, the saponification number reaches a definite maximum of 230 to 231 which is independent of the strength of alkali for all the cases studied. It is clear that in no case is complete saponification obtained in a half hour.

TABLE I. RATE OF SAPONIFICATION USING 0.5 *N* POTASSIUM HYDROXIDE

Time of refluxing, hours	0.25	0.5	0.75	1	2	3
Saponification number	206.6	213.0	224.9	226.8	230.2	231.0
	205.5	216.4	225.0	226.3	230.1	230.0
	204.5	215.8	224.8	226.0	229.8	231.0
Av.	205.5	213.9	224.9	226.3	230.0	230.6

TABLE II. RATE OF SAPONIFICATION USING 1.0 *N* POTASSIUM HYDROXIDE

Time of refluxing, hours	0.25	0.5	0.75	1	2	3	4	6
Saponification number	211.3	223.3	227.8	230.0	229.8	231.1	231.8	231.7
	211.5	223.0	227.9	230.0	228.6	230.9	231.1	231.3
	211.6	223.5	227.8	231.0	228.6	230.0	231.8	231.9
Av.	211.4	223.3	227.8	230.3	229.0	230.6	231.8	231.6

TABLE III. RATE OF SAPONIFICATION USING 2.0 *N* POTASSIUM HYDROXIDE

Time of refluxing, hours	0.5	1	2	3	4
Saponification number	199.6	208.6	217.7	230.0	228.9
	198.3	202.8	217.1	229.0	228.6
Av.	199.2	206.7	217.4	229.5	228.7

After a rapid initial saponification, the reaction proceeds as a straight-line function. Since saponification numbers are proportional to the amount of shellac which has reacted, we are in the position to state that this final saponification proceeds as a bimolecular reaction where the reciprocal of concentration is directly proportional to time. This is exactly what one would expect during the saponification of an ester.

Considering what is already known of the constitution of shellac, the results may be explained on the basis of saponification proceeding in three distinct stages: (a) immediate neutralization of free acid groups, (b) hydrolytic cleavage of easily saponifiable ester bonds such as occurs in lactide or anhydride linkages, and (c) bimolecular saponification of an intra-ester type.

The shellac studied here contained 8.3 per cent of extraneous matter, as insoluble, wax, and moisture. It gave an acid number of 70.2 when 5 grams were dissolved in 50 cc. of neutral alcohol and the acidity determined by titrating with standard 0.5 *N* alcoholic alkali, using thymol blue as outside indicator. On the basis of resin content, this shellac would

then have an acid number of 76.4, a saponification number of 250.9, and an ester number of 174.5.

If we assume shellac to be composed of condensation products of approximately the same molecular weight, we would then expect to have a stoichiometric relationship between the acid number and the ester number. For an ester number of 171.5 this would require an acid number of 58.2 and give a calculated molecular weight of 962.2. The higher acid number of this shellac could be interpreted as representing the possible presence of extraneous acids, such as palmitic acid, found by Gupta (5).

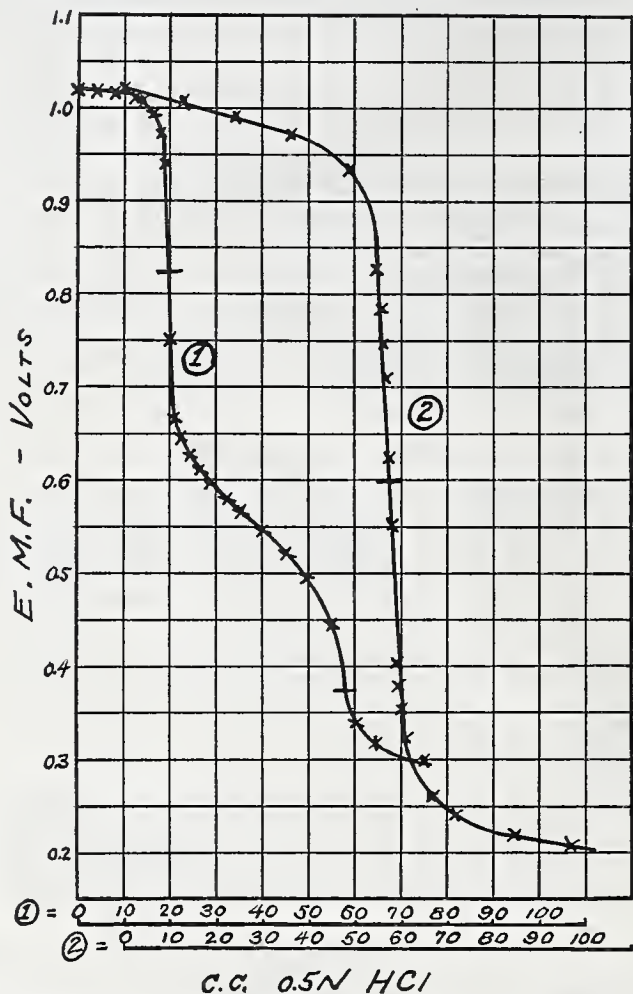


FIGURE 2. TITRATION CURVE OF SAPONIFIED SHELLAC. 1, Saponified shellac solution; 2, potassium hydroxide

On this basis, 192.8 would represent the hydrolytic cleavage of two ester bonds such as would take place when a lactide is saponified. It can be seen from the curves that the intercepts of the straight lines approximate this figure, and the rapid initial saponification might be so interpreted.

Just why the saponification should proceed more slowly with 2 *N* than with 0.5 *N* and 1.0 *N*, our present knowledge will not permit us to answer. It may be possible that in these more concentrated solutions certain colloidal effects are present, such as McBain (10) has observed for alkali soaps of the fatty acids, which may lower the initial concentration of the reactants, even if a greater amount of alkali is present.

POTENTIOMETRIC TITRATION OF SAPONIFIED SOLUTIONS

Since there might be some doubt as to the accuracy in obtaining the true end point when using thymol blue and aqueous hydrochloric acid for titrating the excess of alkali, saponified solutions were titrated potentiometrically to test the contentions of Nagel and Körchen (12).

The experimental conditions in titrating these solutions are similar to those in titrating the acidity of shellac (4). Full details are given in the paper describing that method. A

typical titration curve for these solutions is shown in Figure 2. When a complete titration curve is desired, such as that shown, it is essential that all traces of arsenious sulfide, orpiment which usually occurs in small amounts as an adulterant, be removed before the shellac is saponified. This can be accomplished by dissolving the shellac in alcohol and carefully filtering the solution before the alkali is added. When this is not done, hydrogen sulfide is generated as the solution becomes acid and the hydrogen electrode is poisoned.

It can be seen from the curve that a very sharp point of inflection occurs where the excess of alkali has just been neutralized. This point corresponds exactly to the value obtained with thymol blue, and leaves no doubt as to the sharpness with which the end point can be measured.

The second inflection represents the completion of the titration of the salts of the weak constituent hydroxy-acids by the strong hydrochloric acid. This inflection exactly corresponds to the acidity of the saponified acids, which can be calculated from the saponification number. If any of the acids formed on saponification were strong acids in alcohol, such corresponding results would not be obtained, and it is very unlikely that as sharp an inflection, if any, would be obtained for a titration curve. This inflection corresponds approximately to the change in color of methyl orange or bromothymol blue.

SAPONIFICATION NUMBERS OF VARIED GRADES OF SHELLAC

This study has definitely established that in the case of the superfine orange shellac used, refluxing for at least 2 hours is required for complete saponification when 0.5 *N* alkali is used, and that aqueous hydrochloric acid may be employed for back titration with thymol blue as outside indicator. Aqueous hydrochloric acid has the marked advantage of not changing its titer, which is not true with strong alcoholic acid solutions. Accordingly, the saponification numbers of orange, garnet, and bleached shellac and seedlac were then determined using the previously described method and incorporating these modifications. Duplicates were refluxed for 3 hours to make sure that complete saponification was obtained in all cases. For the purpose of comparison, values were obtained by the common method of refluxing for half an hour.

The results are summarized in Table IV. It can be seen from this table that in no case was complete saponification obtained with half an hour's refluxing, and that the new method gives relatively more constant numbers.

TABLE IV. SAPONIFICATION NUMBERS FOR VARIED GRADES OF SHELLAC

SAMPLE	SAPONIFICATION NUMBER WITH REFLUX OF:		
	0.5 hr.	2 hrs.	3 hrs.
T. N. orange	211.29	225.0 225.6	224.3
U. S. S. I. A. heart orange	227.3	234.1 232.8	234.1
Superfine orange	216.58	230.2 230.1	230.6
A. S. O. orange	222.5	229.8 230.0	230.0
Garnet lac	211.2	222.7 222.62	223.5
Seedlac	220.6	224.6 225.9	225.9
Seedlac	208.5	220.1 220.9	220.9
Bleached shellac	252.9	259.0 258.6	259.6
Refined bleached shellac	253.2	258.6 258.3	258.6

It is of interest to note that in the case of bleached shellac the saponification numbers are considerably higher than those of the orange grades, but this increase corresponds to an increase in the acid number. It would appear from this that in the bleaching process, some of the hydroxyl groups have

TABLE V. NUMBERS FOR DIFFERENT VARIETIES OF SHELLAC CALCULATED ON BASIS OF RESIN

SAMPLE	Hot- Alcohol Insoluble	WAX	MOISTURE	RESIN	ACID No.	SAPONIFI- CATION No.	ESTER No.	RESIN BASIS		
	%							Acid no.	Saponifi- cation no.	Ester no.
T. N. orange	2.32	5.07	0.94	91.67	72.9	225.3	152.4	79.5	245.7	166.2
Heart orange	2.29	4.88	1.01	91.82	75.0	234.1	159.1	81.6	254.8	173.2
Superfine orange	2.20	5.00	1.11	91.69	70.1	230.1	160.0	76.4	250.9	174.5
A. S. O. orange (special)	0.66	5.00	0.94	95.40	73.9	230.0	156.1	77.4	241.0	163.6
Seedlac	6.20	5.00	1.33	87.47	70.6	225.9	155.3	80.7	258.2	177.5
Seedlac	5.34	5.08	1.26	88.32	69.6	220.9	151.3	78.9	250.1	171.2
Bleached shellac	0.01	4.91	0.90	94.18	93.6	259.0	166.4	99.4	275.6	176.6
Refined bleached shellac	0.01	0.20	2.33	97.46	107.5	276.0	168.5	110.6	283.7	173.1

probably been oxidized to carboxyl groups, but that on the whole the molecules, as indicated by the ester number, remain unchanged.

Table V gives values for the corrected acid, saponification, and ester numbers on the basis of resin content as calculated from the percentages of insoluble matter, wax, and moisture. The analyses were made in accordance with the methods given in the Booklet of Official Methods of Analysis of the United States Shellac Importers' Association, Inc., and the American Bleached Shellac Manufacturers' Association, Inc. (1930). The values for corrected ester numbers are surprisingly uniform for a substance of this type, especially when one considers the variety of conditions to which different samples have been subjected in their manufacture. It is an index of the remarkable stability of this commodity. These numbers can be used for identifying a resin as shellac. Although contrary to general practice, a calculation of these chemical constants on the basis of resin content, rather than on total weight of sample, is recommended for identification purposes.

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Silver in Lead Bullion

Determination by Volumetric Method

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TO DETERMINE silver in lead bullion by the volumetric method, weigh three sets of two lead gum drops, flattened to hasten dissolving. Place in a 400-cc. beaker and add 10 grams of tartaric acid to keep antimony in solution, then add enough nitric acid so that there is 1 cc. of acid for each gram of lead present, and then add three times as much water (free from chlorine) as acid.

After the lead is dissolved, dilute to about 250 cc. with cold distilled water, and cool. Add a slight excess of ammonium sulfocyanate solution to precipitate the silver as silver sulfocyanate. After stirring vigorously, let it stand for about 15 minutes and then filter through a double S & S 604 paper. Wash about eight times with cold water.

Flatten the filter paper against the side of the beaker and wash the precipitate into the beaker with cold water, then with cold concentrated ammonia (about 25 cc.). Make sure the precipitate is off the paper. Stirring with a rod will hasten the dissolving of the silver sulfocyanate. Do not heat. After all the silver sulfocyanate is dissolved, dilute to about 200 cc. with cold water.

Make slightly acid with hydrochloric acid, stir vigorously, and filter through double S & S 604 paper. Wash three

times. Add 5 cc. of hydrochloric acid to the filtrate, dilute to about 400 cc., and titrate with permanganate.

It will be noted from the table that the results vary somewhat with the fire and combination methods. This is due to scorification and cupellation losses and the varying amounts of bismuth these lots carried.

SOLUTIONS REQUIRED

Ammonium sulfocyanate, 1 cc. = 10 mg. of silver
Permanganate, 1 cc. = 1 mg. of silver

Note. Fire assay will show how much sulfocyanate to add; all water must be free from chlorine until silver is precipitated as a chloride. Standard to be run is the same as bullion using 30 grams of c. p. lead and weighed amount of c. p. silver equivalent to approximate assay of bullion.

SILVER DETERMINED BY VARIOUS METHODS

(Measurements in troy ounces per ton)

LOT	TITRATION		FIRE	WET + FIRE
	Chemist 1	Chemist 2		
A	58.0	57.9	57.3	56.2
B	53.4	53.3	53.2	52.1
C	55.0	55.6	54.7	53.8
D	50.3	50.2	48.9	47.8
E	53.0	52.6	51.6	50.9

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Potentiometric Determination of Acid Number of Linseed Oil and Its Free Fatty Acids

Comparison of Results Obtained in Different Solvents by Indicator and Potentiometer Methods

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THE manufacturers of paints, enamels, and inks are often confronted with the problem of livering. Pigmented coatings, when first ground, will flow freely from one container to another but, after several days' standing, the coating may not flow at all. The material has changed from a free-flowing viscous liquid to a plastic body of buttery consistency. This change is called livering.

The rate at which the change takes place varies with different pigments as well as with different vehicles. Some mixtures of pigment and vehicle liver while grinding.

For some time the acid number of the vehicle was blamed for this effect; the higher its acid number the more rapid the change, in general. But this is not always true. Occasionally vehicles with high acid number give excellent coatings.

This fact suggests that possibly hydrogen-ion concentration rather than total acidity may be responsible for this change in so far as it is brought about by the vehicle.

The A. S. T. M. method (1) for determining the acid number of an oil indicates total acidity, but tells nothing about hydrogen-ion concentration.

The most important acids present in linseed oil are: linolenic, linolic, and oleic, with smaller quantities of stearic and palmitic.

SOLVENTS USED

The A. S. T. M. method (1) employs as solvent ethyl alcohol, and the solution is titrated with alcoholic potash using phenolphthalein as indicator. Holde (4) suggests as solvent a mixture of two parts of benzene to one of ethyl alcohol, by volume, and Alkali Blue 6B as indicator. Seltz and McKinney (5) use amyl alcohol as solvent and a potentiometric indication of the end point in the titration. Gardner and Whitmore (3) in this laboratory have shown the utility of potentiometric titration in non-aqueous solvents in connection with their work on shellac, and their titration curves, like those of Seltz and McKinney for weak acids in non-aqueous solvents, are surprisingly like those of strong acids in water. The same fact is evident in this work.

Ethyl alcohol would naturally be first selected for this work on account of its being easily obtained in pure condition, and especially on account of its similarity in many respects to

THE RESULTS of determining the acid value of raw and heat-bodied linseed oil by potentiometric titration are presented, as well as the potentiometric determination of the end points in titration of stearic, oleic, and linolenic acids, and the mixed free fatty acids of linseed oil. Ethyl alcohol, 95 per cent, amyl alcohol, butyl alcohol, and an equal-volume mixture of benzene and ethyl alcohol are used as solvents, the last being preferred.

The greater dependability of the quinhydrone electrode over the hydrogen electrode is shown, and comparison of end points and acid numbers thus gotten with those obtained using phenolphthalein is made. While dissociation constants for the acids in these non-aqueous solvents have not been obtained, the results warrant the arrangement of the acids in order of decreasing strength, as follows: stearic, oleic, mixed linseed fatty acids, linolenic. The work was undertaken in connection with a study of the problem of livering, which is still in progress.

water. Furthermore, solutions in ethyl alcohol should be better conductors than those in higher alcohols, and the internal resistance of such cells would not be too high for easy e. m. f. measurement. However, it soon developed that because of the rather poor solubility of linseed oil in 95 per cent ethyl alcohol, other solvents had to be used. Butyl alcohol, as well as amyl alcohol, was tried, but finally it was found that a solvent consisting of benzene and ethyl alcohol, as suggested by Holde, was to be preferred to any that had been tried. However, equal volumes of the two liquids were used.

The 95 per cent ethyl alcohol was redistilled from potassium hydroxide and a small amount of silver nitrate. The butyl alcohol was especially redistilled for the purpose by the Commercial Solvents Company, and again distilled just before use from potassium hydroxide and silver nitrate. The amyl alcohol, also, was purified by redistillation.

APPARATUS

The apparatus consisted of a Leeds and Northrup hydrogen-ion potentiometer, galvanometer, lamp, and scale. The potentiometer had a range from 0 to 1.61 v., and an accuracy of 0.5 mv. with resistance less than 10,000 ohms. The galvanometer had a sensitivity of 40 megohms and a period of 3 seconds.

The hydrogen electrode first employed, but later discarded, was of the Hildebrand type prepared as directed by Clark and others. All the work hereafter recorded was, however, done with the quinhydrone electrode, since the length of time with the former electrode to establish a constant reading sometimes exceeded 30 minutes, and it was quickly poisoned in the solution.

Britton (2) has summarized the chief advantages of the quinhydrone electrode, stating among other advantages its quickness in attaining equilibrium, its frequent dependable use in solutions containing oxidizing agents, and its greater resistance to incapacitating reactions than the hydrogen electrode.

Among its disadvantages is the fact that it does not give constant readings in solutions more alkaline than pH 8.

The reference electrode used was a calomel half-cell containing a saturated solution of lithium chloride in ethyl alco-

hol. Two such half-cells were prepared which, when used against the same hydrogen electrode in a titration of 0.1 *N* Bureau of Standards benzoic acid, gave nearly identical results.

The cell whose e. m. f. was to be measured was, then:

Hg	Hg ₂ Cl ₂ + sat. soln. LiCl in 95% ethyl alcohol	salt bridge of sat. soln. of LiCl in 95% ethyl alcohol	soln. of acid or oil in 95% ethyl, amyl, butyl, or benzene-ethyl alcohol mixture, containing quinhydrone	Au
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The titration vessel consisted of a 200-cc. cylinder fitted with rubber stopper bearing inlets for buret, calomel half-cell, stirrer, stream of nitrogen, quinhydrone electrode (gold), and outlet opening. A drop of saturated alcoholic solution of quinhydrone was added to the titrating vessel for each 10 cc. of solution, whatever the solvent in use. The nitrogen stream served the purpose of excluding air from the titration vessel.

PROCEDURE

The acids examined were sulfuric and benzoic acids, for comparison, and stearic, oleic, linolenic, and mixed linseed fatty acids. In addition, heat-bodied and raw linseed oils were titrated. (Further work on acid values of heat-bodied oils is reported in another paper soon to be published.) The oils were digested with the solvent on a steam bath with reflux condenser, then cooled and titrated. The free acids were titrated without refluxing.

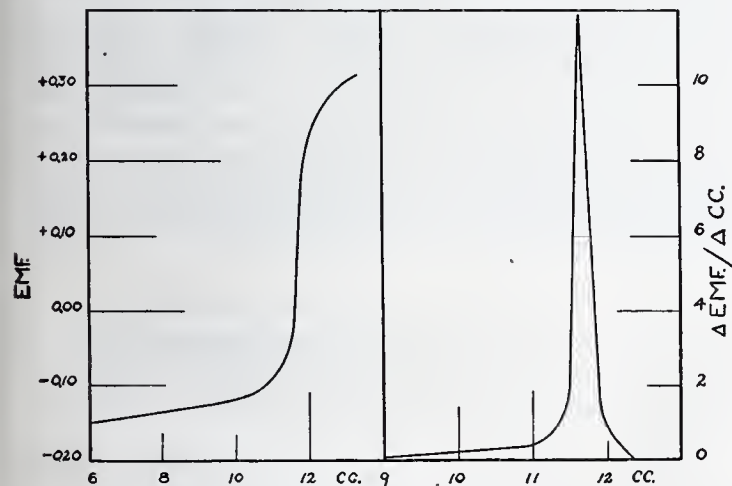


FIGURE 1. BENZOIC ACID IN BUTYL ALCOHOL

A 150-cc. portion of solvent was used in the study of the free acids in benzene-ethyl alcohol solution, nearly twice the amount required to dissolve them. With amyl and butyl alcohols as solvents, 100 cc. were employed.

In the earlier work using the hydrogen electrode, hydrogen was passed rapidly through the solution for 15 minutes or more before titration was started, then at the rate of one bubble per second. Apparent constancy was awaited before recording the potentiometer reading. Sometimes 40 minutes passed, but toward the neutral point constancy was obtained more quickly.

When the quinhydrone electrode was used, nitrogen was passed at the rate of one bubble per second through the solution after it had become saturated by preliminary bubbling for 20 minutes. Constancy of reading could be obtained in less than 5 minutes, but a longer time was allowed before recording and adding the next increment of base. After passing the neutral point, when the pH value of the solution was high (above 8.5), the voltage would drop, so shorter time periods

were allowed. This part of the titration is, of course, unimportant.

SOLUTIONS IN 95 PER CENT ETHYL ALCOHOL

(a) To standardize the alcoholic potash, a 0.1 *N* solution of Bureau of Standards benzoic acid was prepared and titrated. Four titrations were run, three giving identical results with end point at 10.00 cc. of 0.1 *N* potassium hydroxide for neutralization of 10 cc. of 0.1 *N* acid. The fourth titration gave 9.92 cc. of 0.1 *N* potassium hydroxide.

The curve has the form of a titration curve for a strong acid in water, there being a change of approximately 0.15 volt for addition of only 0.1 cc. of base.

(b) Exactly 10 cc. of 0.1 *N* stearic acid were titrated, giving a sharp inflexion, but not so sharp as for benzoic acid, the change in e. m. f. per 0.1 cc. at the neutral point being not so great. The neutral point was practically the same for a number of titrations at 9.95 cc. of base.

(c) End points for oleic acid were reached as follows:

INDICATOR	POTENTIOMETER
Cc.	Cc.
9.85	9.80
	9.82

(d) Exactly 10 cc. of 0.1 *N* linolenic acid were titrated with the following results:

INDICATOR	POTENTIOMETER
Cc.	Cc.
9.84	9.86
9.84	9.83

(e) For approximately 0.1 *N* sulfuric acid, the curve has the form of a strong monobasic acid in water. The end point is at 9.85 cc., indicator 9.90 cc.

(f) Mixed linseed fatty acids, of acid number 179.0, gave a very regular curve characteristic of a moderately strong single acid. Indicator end point gave acid number 180.

SOLUTIONS IN BUTYL ALCOHOL

(a) To ascertain whether constant acid numbers could be gotten under large concentration changes, the following titrations were run, all on the same oil:

WEIGHT OF OIL	ACID VALUE
Grams	Cc.
10	5.06
10	5.01
5	5.03
5	4.96

(b) To ascertain whether the form of the titration curves would be noticeably different for two heat-bodied linseed oils which had been brought to the same approximate acid number (acid number 7) at different temperatures, titrations were run on an oil bodied at 287.7° C. (550° F.) and on one bodied at 301.6° C. (575° F.).

TEMPERATURE OF HEATING OIL		ACID VALUE	
		Indicator	Potentiometer
° C.	(° F.)	Cc.	Cc.
287.7	(550)	7.46	7.41
			7.48
301.6	(575)	7.35	7.16
			7.27

The curves had practically the same form.

(c) It may not be amiss to record some end-point figures for a titration of benzoic acid in butyl alcohol, for comparison. These were obtained from color change of phenolphthalein in the ordinary way, from the mid-point of the vertical portion of the potentiometric-titration curve in which the usual plot of volts against cubic centimeters of base has been employed, and also from a differential titration curve in which Δ (e. m. f.) / Δ cc. reaches a sharp maximum at the end point.

METHOD	RESULT
Indicator	Cc.
E. m. f./cc.	11.65
$\Delta(e. m. f.)/\Delta cc.$	11.60
	11.63

Figure 1 shows these results graphically.

While the differential method is more accurate for determining the end point of a neutralization, it does not have to be used in work of this kind since the vertical part of the ordinary titration curve is quite long.

The conductivity of butyl alcohol solutions is much poorer than that of ethyl alcohol systems. With amyl alcohol as solvent, the results are practically identical with those in butyl alcohol, so that there is no need for special comment.

SOLUTIONS IN BENZENE-ETHYL ALCOHOL MIXTURE (EQUAL VOLUME)

On the whole, the solvents last named are not so good for linseed oil as the benzene-ethyl alcohol mixture, as the following results prove:

ACID	END POINTS	
	Indicator	Potentiometer
	Cc.	Cc.
Benzoic	10.20	10.29
Linolenic	8.22	8.20
Sulfuric	10.75	10.72
ACID NUMBER		
	Indicator	Potentiometer
Mixed linseed fatty acids	178.26	178.75
		179.88
In ethyl alcohol		179.00
In butyl alcohol		179.00
		179.28
		179.94

For linseed oil in the mixed solvent, the acid numbers are:

INDICATOR	POTENTIOMETER
Cc.	Cc.
7.35	7.38
	7.40
	7.43

The same for an acid refined raw oil are 2.53 and 2.83.

RELATIVE STRENGTHS OF ACIDS

If we arrange the acids studied in order of decreasing strength, judging from the character of the titration curves and also from the values for the electromotive force at the half-neutralization point, the order is the same, as follows:

ACID	VOLT
Sulfuric	0.270
Benzoic	0.155
Stearic	0.149
Oleic	0.137
Mixed linseed fatty	0.125
Linolenic	0.125

It is of course recognized that the e. m. f. values are not direct measures of the relative strengths of the acids, but they are related to them.

According to the mass action law, if a monobasic acid HA ionizes into H^+ and A^-

$$K_a = \frac{(H^+)(A^-)}{(HA)}$$

where K_a is the ionization constant of the acid. At the half-neutralization point, on the assumption of complete ionization of the salt and zero ionization of the acid in the presence of its salt,

$$\frac{(A^-)}{(HA)} = 1$$

hence

$$K_a = (H^+)$$

That is to say, the ionization constant of the acid has a numerical value equal to the concentration of hydrogen ions

in the half-neutralized solution of the acid. In view of our lack of information concerning electrode potentials of the calomel electrode in saturated lithium chloride alcoholic solution and the magnitude of the liquid junction potentials here encountered, we are not able to calculate the hydrogen-ion concentration. But other factors being constant, the e. m. f. is a logarithmic function of the H^+ , so that we are justified in the use of e. m. f. values in making the above arrangement of the acids in the serial order of their decreasing values of K_a .

Figures 2 and 3 show titration curves for these acids in ethyl alcohol and in the benzene-alcohol mixture.

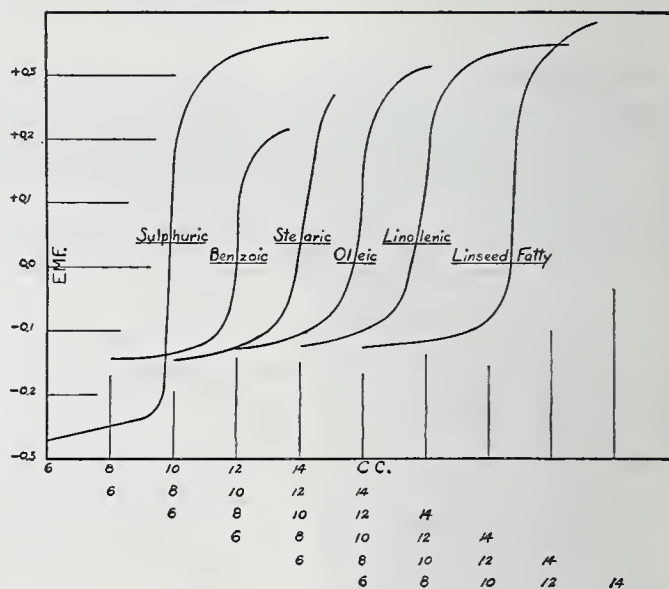


FIGURE 2. TITRATION CURVES OF ACIDS IN ETHYL ALCOHOL

Figure 4 shows titration curves for a single heat-bodied linseed oil in 95 per cent ethyl alcohol-benzene mixture with points obtained in three titrations made at different times. It will be noted that although the curves differ from one another, they practically coincide in the inflection portion. The acid values calculated from the three end points are 7.38, 7.40, and 7.43. By titration with phenolphthalein, the value gotten was 7.35.

EXTRACTION OF FREE FATTY ACID

Some experiments were performed with the several solvents above mentioned with the object of learning the behavior of each in extracting the free fatty acids from heat-bodied linseed oils.

(a) The oil used in this set of determinations was bodied at $329.5^\circ C.$ ($625^\circ F.$) to an approximate acid value of 14.

Approximately 10 grams were refluxed for a half hour on the water bath with 50 cc. of the equal-volume mixture of benzene and 95 per cent ethyl alcohol, then cooled and titrated.

Acid value: 14.39 14.38

Another 10-gram portion of the same oil was refluxed in the same way with 50 cc. of 95 per cent ethyl alcohol. The oil was not completely dissolved or dispersed. The mixture was stirred every 3 to 5 minutes, but on standing it quickly separated into two layers. The whole was cooled, mixed, and titrated.

Acid value: 14.36 14.39

A third 10-gram portion of the same oil was refluxed as above with 50 cc. of butyl alcohol. When hot the oil seemed completely dispersed, but on cooling the mixture clouded and partially separated into two layers, though not as distinctly as in the case above. The whole was cooled, mixed, and titrated.

Acid value: 15.06 14.99

A fourth sample was treated as above with 50 cc. of amyl alcohol. It acted as with butyl alcohol.

Acid value: 14.67 14.74

(b) The same oil as was used above was used in another series of experiments.

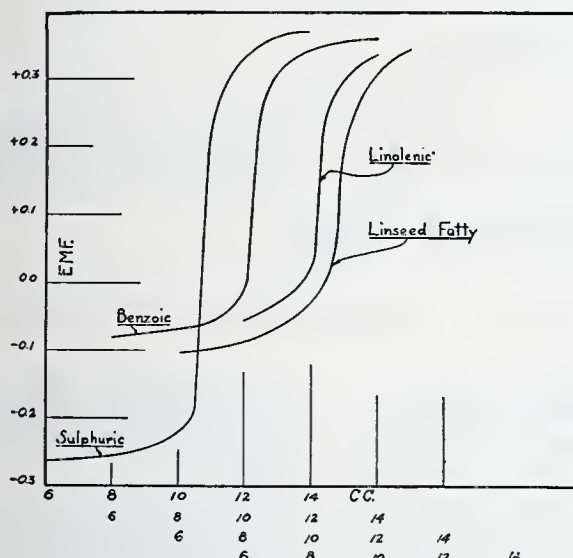


FIGURE 3. TITRATION CURVES OF ACIDS IN BENZENE-ETHYL ALCOHOL MIXTURE

Approximately 10 grams were refluxed for a half hour on the water bath with 50 cc. of 95 per cent ethyl alcohol. The mixture was cooled and the alcohol decanted. The residue was washed with three separate 10-cc. portions of alcohol, each being decanted. All alcohol decantations were collected and titrated.

Acid value: 8.83 8.46

To the residue were added 50 cc. of the equal-volume mixture of benzene and 95 per cent ethyl alcohol, and the solution was refluxed for a half hour on the water bath, cooled, and titrated.

Acid value: 5.27 5.93
Total acid value: 14.10 14.39
Fraction of total acid removed by ethyl alcohol: 62.6% 58.8%

Alcohol washings in a similar experiment gave

Acid value: 8.71 8.21

The residue was not further treated.

The oil used here was a different one. It had been bodied at 329.5° C. (625° F.) to an acid value of about 15. The treatment was as described in (b), paragraph 1.

Acid value (alcohol extract): 10.18 10.33
Acid value (residue): 4.86 4.91
Total acid value: 15.04 15.24
Fraction of total acid removed by ethyl alcohol: 67.7% 67.7%

(c) An oil bodied at 287.7° C. (550° F.) to an acid value of approximately 8 was treated as in (b), paragraph 1.

Acid value (alcohol extract): 4.70 5.05
Acid value (residue): 3.39 3.15
Total acid value: 8.09 8.20
Fraction of total acid removed by ethyl alcohol: 58.1% 61.5%

(d) The same oil as that used in (b), paragraph 1, was refluxed for three successive half-hour periods over the water bath with 40, 30, and 20 cc. of 95 per cent ethyl alcohol. After each refluxing the alcohol was decanted. The residue

was washed with 10 cc. more of alcohol. All alcohol decantations were collected and titrated.

Acid value (alcohol extract): 9.37 9.52
Acid value (residue): 4.77 4.78
Total acid value: 14.14 14.30
Fraction of total acid removed by ethyl alcohol: 66.3% 66.6%

The per cent removed by three refluxings with ethyl alcohol was only a little greater than when the extraction was made as in (b), paragraph 1.

(e) This oil was bodied at 301.6° C. (575° F.) to an acid value of around 7. The treatment was as described in (d).

Acid value (alcohol extract): 5.26 4.86
Acid value (residue): 2.63 2.90
Total acid value: 7.89 7.76
Fraction of total acid removed by ethyl alcohol: 66.6% 63.4%

(f) This oil was bodied at 287.7° C. (550° F.) to an acid value of approximately 8. To 50 grams of oil were added 2 grams of mixed linseed fatty acid. The mixture was treated as in (d).

Acid value (alcohol extract): 14.83 14.78
Acid value (residue): 2.46 2.47
Total acid value: 17.29 17.25
Fraction of total acid removed by ethyl alcohol: 85.7% 85.7%

The above experiments show that the equal-volume mixture of benzene and ethyl alcohol is the best solvent of those employed, that ethyl alcohol alone dissolves approximately two-thirds of the acids present in bodied linseed oils, the remainder

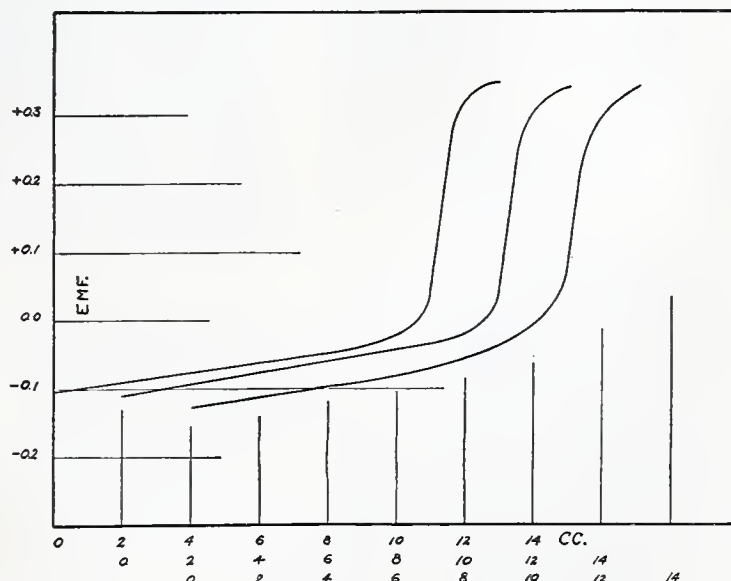


FIGURE 4. TITRATION CURVES OF BODIED LINSEED OIL

being tenaciously held, probably adsorbed on the gel particles. It appears that mixed linseed fatty acids are more soluble in alcohol than other acids formed in processing, but in their removal carry along a small amount of acid which would otherwise remain undissolved. Further work on this point is now in progress.

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Elimination of Corrections for Nitrites in Nitrate Determinations

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IN A previous report (2) it was suggested that nitrite nitrogen could be completely eliminated without affecting the nitrate nitrogen by evaporation of a neutral solution to dryness in the presence of an excess of ammonium chloride. This was suggested for the reduction method for the purpose of eliminating the troublesome correction for nitrites.

The following report deals with the influence of reaction and certain ammonium salts on the success of the proposed method.

REACTION LIMITS IN EVAPORATION TO DRYNESS

Portions of solution (50 cc.) containing various quantities of nitrites and nitrates acidified with acetic acid, as shown in Table I, were evaporated to dryness on a water bath, and the residue dissolved in 100 cc. of nitrogen-free water. Fifty cubic centimeters were then tested for nitrites with naphthylamine acetate, and the nitrogen in the remaining 50 cc. was determined by the reduction method. To bring the reaction to a pH of 1.9 it was necessary to add some hydrochloric acid. It is evident that at this reaction both nitrite and nitrate were decomposed on evaporation.

At reactions of pH 3.0 to 3.2, nitrites up to 9.20 parts per million were decomposed completely, whereas nitrates were not affected, the latter being quantitatively recovered.

At reactions of pH 4.0 or more alkaline (observations were made up to pH 7.9), neither nitrites nor nitrates were lost.

These results indicated the possibility of eliminating the corrections necessitated through the presence of nitrites by the simple process of adjusting the reaction to a pH of 3.0 and evaporating to dryness. A series of observations was therefore undertaken with other acids to ascertain whether this limiting reaction was applicable when employing hydrochloric, sulfuric, or phosphoric acids.

The results for these three inorganic acids are summarized in Table II. It appears that, as was observed with acetic acid, the nitrites were destroyed when evaporated to dryness from solutions made up to a pH of 3.0 with sulfuric or phos-

THE LIMITING reactions at which nitrites and nitrates are decomposed on evaporation to dryness have been determined. Nitrites are decomposed at pH 3 and nitrates at pH 2 when acidified with acetic acid. It has been observed that nitrites are destroyed by evaporation to dryness in the presence of ammonium chloride or ammonium sulfate from acid or moderately alkaline solution, but at pH 11 none of the nitrite was lost. Ammonium hydroxide and ammonium carbonate did not serve to decompose the nitrite on evaporation. The elimination of the troublesome correction for nitrites in the determination of nitrates by evaporation of a neutral solution in the presence of ammonium chloride or ammonium sulfate, and the possibility of utilizing a solution made acid (pH 3), with acetic acid for this purpose, is suggested.

phoric acids, but with hydrochloric a reaction of pH 2.7 was required.

With respect to the stability of nitrates, however, the results (Figure 1) were quite different from those observed with acetic acid. Thus, with hydrochloric acid there was no loss of nitrates at pH 3.0. At this reaction, however, nitrite was not always completely destroyed. At a reaction of pH 2.8 with hydrochloric acid, there was a loss of over 13 per cent of nitrates, and at pH 2.7, which was found necessary to destroy nitrites, there was a loss of over 50 per cent of nitrates.

With sulfuric acid, the results were even more discouraging. It was found that at pH 3.2, there was a loss of 16 per cent,

and at pH 3.1 over 70 per cent of nitrates were destroyed on evaporation to dryness.

TABLE I. EFFECT OF ACETIC ACID ON RECOVERY OF NITRITE AND NITRATE AFTER EVAPORATION TO DRYNESS

INITIAL REACTION pH	NITROGEN Nitrite P. p. m.	ADDED Nitrate P. p. m.	QUAL. TEST FOR NITRITE	NITROGEN RECOVERED P. p. m.	REMARKS
1.9 ^a	..	4.59		1.05	Nitrate destroyed
1.9 ^a	4.60	4.61		1.60	Nitrate destroyed
3.0	..	4.59		4.60	Nitrate recovered
3.0	41.70	Nitrite destroyed
3.1	1.84	Nitrite destroyed
3.2	9.20	Nitrite destroyed
3.1	4.60	4.61		4.63	Nitrite destroyed, nitrate recovered
4.0	1.84	..	+	..	Nitrite present
4.1	9.20	..	+	..	Nitrite present
4.0	..	4.59		4.74	All nitrate recovered
4.0	4.60	4.61	+	9.29	Both nitrite and nitrate recovered
5.4	4.60	4.61	+	9.28	Both nitrite and nitrate recovered

^a A small quantity of hydrochloric acid had to be added to bring reaction to pH 1.9.

The results with phosphoric acid showed losses of 98 per cent at pH 2.8, 73 per cent at pH 3.0, 34 per cent at pH 3.2, and about 4 per cent at pH 3.4. In general there was an overlapping of the reaction at which nitrites and nitrates were destroyed on evaporation from solutions made acid with these

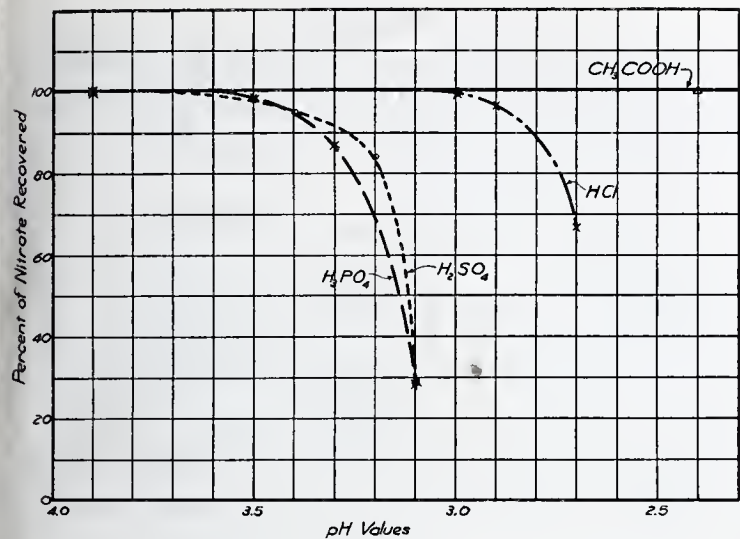


FIGURE 1. RECOVERY OF NITRATES FROM VARIOUS ACID SOLUTIONS

mineral acids. The reaction was quite in marked contrast to that observed with acetic acid, where pH 3.0 was found to form a sharp line of demarcation at which nitrites were completely destroyed while nitrates were not affected. It is therefore suggested that acidification with acetic acid to pH 3.0 (avoiding too large an excess of the acid) and evaporation to dryness may be employed for elimination of nitrites in the determination of nitrates. It was found on further study that this method could not be safely employed if the initial concentration of nitrites was over 20 parts per million, because of an apparent oxidation of some of the nitrites to nitrates.

TABLE II. EFFECT OF MINERAL ACIDS ON RECOVERY OF NITRITES AND NITRATES AFTER EVAPORATION TO DRYNESS

INITIAL REACTION pH	HYDROCHLORIC ACID		SULFURIC ACID		PHOSPHORIC ACID	
	Amt. added P. p. m.	Qual. test	Amt. added P. p. m.	Qual. test	Amt. added P. p. m.	Qual. test
EXPERIMENTS WITH NITRITES						
2.7	9.2					
2.7	19.7					
2.7	27.2	Trace				
2.7	47.2	Trace				
3.1	9.1		8.9		9.21	
3.1	27.2	+	42.4			
3.3	8.8				9.21	
3.3	9.2	+				
3.3	16.6	+				
3.5	9.2	+	8.9	+	9.21	+
3.7	9.2		8.9	+	9.21	+
EXPERIMENTS WITH NITRATES						
		Nitrogen recovered		Nitrogen recovered		Nitrogen recovered
2.7	8.78	4.29		8.92	0.15	
2.8	8.97	7.78		8.92	0.42	
2.9	8.98	8.70		8.92		
3.0	8.98	8.98		8.92	2.38	
3.1	8.97	8.97	9.13	2.69	8.92	3.68
3.2			9.13	7.63	8.92	5.88
3.3	8.97	8.97			8.92	7.75
3.4			9.13	8.63	8.92	8.58
3.5					8.92	8.75
3.6					8.92	8.75
3.7			9.13	9.12	8.92	8.92
3.8	8.97	8.97				
3.9			9.13	9.12	8.92	8.90

AMMONIUM CHLORIDE AT DIFFERENT ACIDITIES

A number of determinations were made on the influence of reaction on the recovery of nitrites and nitrates after evaporation to dryness in the presence of ammonium chloride. The reactions were adjusted with acetic acid in the acid range and sodium carbonate in the alkaline range, and 1000 parts per million ammonium as chloride were employed in all tests. The results are summarized in Table III, from which it is seen that at initial reactions of pH 2.0 nitrates were destroyed, and between the range pH 3.0 to pH 7.7 the nitrites only were destroyed. It is therefore important that

the reaction be properly adjusted, but as the range suitable for the purpose is very wide (pH 3.0 to about pH 8.0), the adjustment need not be very delicate.

RELATIVE EFFICIENCIES OF VARIOUS AMMONIUM COMPOUNDS FOR ELIMINATION OF NITRITES

A series of ammonia compounds was tested to determine the effect on recovery of nitrites and nitrates after evaporation. Samples were prepared by making up solutions of nitrites and nitrates to 50 cc. The desired quantities of ammonium compounds were then added, and the mixture evaporated to dryness in casseroles on a steam bath. The casseroles were washed down with water and again evaporated. The residue was taken up in 100 cc. of nitrogen-free water. Fifty cubic centimeters were tested for nitrites and the remainder was made alkaline, reduced, etc., as recommended in standard methods for nitrate determination. The results given in Table IV show clearly that ammonium chloride and ammonium sulfate, the salts of strong acids, were satisfactory, whereas ammonium hydroxide and ammonium carbonate, a salt of a weak acid, were not suitable for the destruction of nitrites. In the experiments with ammonium chloride at different hydrogen-ion concentrations, it was found that the reaction had to be more acid than pH 9.0 in order to eliminate nitrites on evaporation. The failure of the hydroxide and carbonate is attributed to the high initial alkalinity of the solutions.

TABLE III. EFFECT OF REACTION ON RECOVERY OF NITRITES AND NITRATES AFTER EVAPORATION TO DRYNESS IN PRESENCE OF AMMONIUM CHLORIDE

INITIAL RE- ACTION pH	NITROGEN ADDED		NITROGEN		REMARKS
	IN Ni- trites P. p. m.	As Ni- trate P. p. m.	TEST FOR Ni- TRITES P. p. m.	RECOV- ERED AS Ni- TRATES P. p. m.	
2.0	4.60	4.59		2.15	Nitrites and nitrates destroyed
2.1	4.60	4.59		1.60	Nitrites and nitrates destroyed
3.0	4.60	4.61		4.68	Nitrites destroyed Nitrates recovered
3.1	None	4.59		4.56	Nitrites destroyed, nitrates recovered
3.9	4.60	4.61		4.43	Nitrites destroyed, nitrates recovered
4.1	4.60	4.59		4.15	Nitrites destroyed, nitrates recovered
4.1	None	4.59		4.50	Nitrates recovered
5.4	4.60	4.61		4.53	Nitrites destroyed, nitrates recovered
5.4	None	4.59		4.70	Nitrates recovered
6.1	4.60	4.61		4.52	Nitrites destroyed, nitrates recovered
6.6	4.60	4.59		4.30	Nitrites destroyed, nitrates recovered
6.9	None	4.59		4.53	
7.0	4.60	None			Nitrites destroyed
7.2	4.60	4.61		4.42	Nitrites destroyed, nitrates recovered
7.6	4.60	4.61		4.52	Nitrites destroyed, nitrates recovered
7.7	4.60	4.61		4.62	Nitrites destroyed, nitrates recovered
11.2	4.60	None	+		Nitrites not destroyed
11.2	4.60	4.61	+	9.25	Both nitrites and nitrates recovered

PROCEDURE FOR DETERMINATION OF NITRATES IN SEWAGE

The following method of determination of nitrates is suggested:

1. Adjust reaction to about pH 7.5. A reaction which is acid to phenolphthalein and alkaline to phenol red will be found satisfactory.
2. Add about 2000 parts per million ammonium as chloride.
3. Evaporate in casserole to dryness on the steam bath. Wash down with distilled water and again evaporate to dryness.
4. Take up the residue in about 100 cc. of distilled water. Add 5 cc. of 40 per cent sodium hydroxide and boil mixture down to about 25 cc. to expel ammonia.
5. Reduce with aluminum foil, distil over the ammonia thus produced, and record as nitrates.

TABLE IV. EFFECT OF DIFFERENT AMMONIUM SALTS ON RECOVERY OF NITRITES AND NITRATES

AMMO- NIUM ADDED	NITROGEN ADDED		QUAL. TEST FOR	NITROGEN	REMARKS
	Nitrites	Nitrates	NITRITES	RECOV- ERED	
<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>		<i>P. p. m.</i>	
AMMONIUM CHLORIDE					
2,000	44.0	8.8	Trace	9.0	Nitrites destroyed Nitrates recovered
2,000	44.7	44.7	Trace	44.7	Nitrites destroyed Nitrates recovered
4,000	47.2	9.4	Trace	9.7	Nitrites destroyed Nitrates recovered
,000	7.2	47.2	Trace	47.2	Nitrites destroyed Nitrates recovered
AMMONIUM SULFATE					
4,000	44.7	8.9	Trace	9.7	Nitrites destroyed Nitrates recovered
4,000	44.7	44.7	Trace	44.7	Nitrites destroyed Nitrates recovered
AMMONIUM HYDROXIDE					
2,000	44.0	8.8	Strong	49.0	Nitrites not eliminated
2,000	44.0	44.0	Strong	79.0	Nitrites not eliminated
4,000	47.2	9.4	Strong	49.7	Nitrites not eliminated
4,000	47.2	47.2	Strong	74.7	Nitrites not eliminated
10,000	44.7	8.9	Strong	53.0	Nitrites not eliminated
10,000	44.7	44.7	Strong	73.0	Nitrites not eliminated
AMMONIUM CARBONATE					
2,000	44.0	8.8	Strong	49.0	Nitrites not eliminated
2,000	44.0	44.0	Strong	79.0	Nitrites not eliminated
4,000	47.2	9.4	Strong	49.7	Nitrites not eliminated
4,000	47.2	47.2	Strong	79.7	Nitrites not eliminated
10,000	44.7	8.9	Strong	47.2	Nitrites not eliminated
10,000	44.7	44.7	Strong	79.3	Nitrites not eliminated

The foregoing method was tried on a number of sewage samples, including creamery and packing-house wastes and domestic sewage. Various quantities of nitrites and nitrates were added to these wastes, which were then treated as described above for recovery of nitrates. The results for a number of tests are summarized in Table V. The method proved to be suitable with the wastes and quantities of nitrites and nitrates employed.

TABLE V. DEPENDABILITY OF NITRITE ELIMINATION PROCEDURE IN DETERMINATION OF NITRATES IN SEWAGE

No. of Detns.	NITROGEN ADDED		NITROGEN FOUND AS NITRATES P. p. m.
	Nitrites P. p. m.	Nitrates P. p. m.	
MADRID RAW SEWAGE			
3	0.0	9.6	9.2
3	9.2	9.6	9.4
3	19.7	9.6	9.5
3	27.2	9.6	9.3
3	47.2	9.6	9.4
AMES TANK EFFLUENT			
4	0.0	9.35	9.20
4	9.2	9.35	9.30
4	19.7	9.35	9.40
4	27.2	9.35	9.50
4	47.2	9.35	9.30
CREAMERY WASTE			
4	9.2	11.86	11.98
3	9.4	30.20	30.15
3	9.4	45.20	44.70
4	19.7	11.86	11.98
4	27.2	11.86	12.23
4	47.2	11.86	11.98
4	46.2	21.45	21.50
4	46.2	30.20	32.20
4	46.2	45.20	44.80
MADRID TANK EFFLUENT			
4	0.0	9.45	9.40
4	9.2	9.45	9.20
4	19.7	9.45	9.50
4	27.2	9.45	9.40
4	47.2	9.45	9.60
AMES FINAL EFFLUENT			
5	0.0	11.8	11.7
5	9.2	11.8	11.7
5	19.7	11.8	11.7
5	27.2	11.8	11.9
5	47.2	11.8	11.7
PACKING-HOUSE WASTE			
4	0.0	9.4	9.34
4	0.0	9.75	9.88
4	9.2	9.48	9.34
4	9.2	9.75	9.75
4	19.7	9.48	9.43
4	19.7	9.75	9.75
4	27.2	9.48	9.50
4	27.2	9.75	9.88
4	47.2	9.48	9.66
4	47.2	9.75	10.38

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Removal of Bromide and Iodide for Detection of Nitrate

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TO DETECT nitrate by the so-called brown ring test, bromide and iodide must first be removed. These halide ions are frequently precipitated by means of saturated silver sulfate or silver acetate solutions and the test made on the filtrate. Since water solutions of these salts are very dilute even when saturated, large volumes must be used if much bromide or iodide is present. It seemed reasonable to expect that a more concentrated solution, made by dissolving the silver salt in ammonium hydroxide, might be employed in this removal. The literature shows no reference to such a method.

A solution 0.5 N with respect to silver sulfate was prepared by dissolving 7.8 grams of the salt (Merck c. p.) in 25 cc. of 4 N ammonium hydroxide and diluting to 100 cc. The solutions tested for nitrate contained 250 mg. of iodide, 100 mg. of bromide, and 70 mg. of chloride per cubic centimeter. The quantity of nitrate was varied from 0 to 1 mg. per cubic centimeter. To 1 cc. of each of these solutions, 3 cc. of 6 N sulfuric acid and a slight excess of ammoniacal silver sulfate solution were added. Approximately 12 cc. of the silver sulfate solution were necessary for complete precipitation of the halides. One cubic centimeter of the filtrate was then mixed with 5 cc. of concentrated sulfuric acid and the mixture cooled and overlaid with a little freshly prepared ferrous sulfate solution. At the end of 5 minutes, solutions containing 0.5 mg. or more of nitrate per original cubic centimeter showed a definite brown ring at the junction of the two layers. Solutions containing less nitrate failed to give satisfactory tests.

By this method it is possible to detect a small amount of nitrate in a solution from which large quantities of bromide and iodide have been removed. Chloride was included, since, if present, it is also removed by the silver ions.

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Dissolved Oxygen in Presence of Organic Matter, Hypochlorites, and Sulfite Wastes

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IN GENERAL, it appears well established that the Rideal and Stewart (14), or permanganate modification of Winkler's well-known procedure for the determination of dissolved oxygen, is of value in dealing with waters containing appreciable quantities of nitrites or of ferrous salts. Likewise, a preliminary treatment with permanganate may be desirable in dealing with such forms of organic matter as are commonly present in freshly aerated sewage at ordinary dilutions or in certain varieties of industrial wastes. However, as shown elsewhere (15), the permanganate modification is of doubtful value in dealing with stale sewage. More recently this widely used modification has been shown to fail when applied to samples containing large amounts of either dextrose or peptone. Certain points of interest in connection with this study will be presented in this paper, and a readily applicable procedure will be developed for the determination of dissolved oxygen in the presence of relatively large amounts of organic matter.

There is another type of interference with the Winkler method for which, on closer study, the permanganate treatment has been found to be of little, if any, value—that is, the interference encountered when dissolved oxygen is determined in the presence of sulfite wastes. Notable amounts of organic matter, as much as 10 per cent by weight, are present in these wastes together with sulfur compounds. A reasonably effective procedure, based on a preliminary treatment with hypochlorites, will be proposed for the determination of dissolved oxygen in the presence of such wastes.

A SIMPLE technic has been developed for the determination of dissolved oxygen by the Winkler method in the presence of large amounts of organic matter.

Attention is called to the error introduced in dissolved oxygen and in oxygen-demand determinations by the decomposition of tetrathionates in highly alkaline solutions.

A new modification of Winkler's procedure is proposed for the determination of dissolved oxygen in the presence of sulfite wastes.

The effect of varying amounts of glucose on the indicated oxygen content of samples containing known amounts of dissolved oxygen is shown in Table I. The experimental solutions were obtained by adding suitable volumes of stock solutions of glucose well below the surface of bottles completely filled with distilled water of known oxygen content. As the concentration of glucose in these stock solutions was relatively high, no correction was

applied for the dilution of the dissolved oxygen. The stoppers were then replaced and the mixture was made uniform by inverting the bottles several times. The usual Winkler reagents (2 ml. each of manganous sulfate and alkaline-iodide solutions) were then added and the bottles were inverted several times to distribute the precipitate. After the precipitate had settled, the bottles were again inverted several times, and when the upper part of the liquid was clear, 2 ml. of concentrated sulfuric acid were added. The test was then completed by titrating a volume of iodine solution equivalent to 200 ml. of the original sample.

In another series of bottles to which corresponding amounts of glucose had been added, the tests were started by a preliminary treatment with permanganate, using 0.7 ml. of concentrated sulfuric acid and enough 0.2 *N* potassium permanganate to produce a reddish coloration which was permanent for 5 minutes. The excess of permanganate was then removed by the addition of minimum amounts of oxalate solution. When decolorization was complete, the regular Winkler reagents (1 ml. of manganous sulfate solution and 3 ml. of alkaline-iodide solution) were added and, after a 5-

TABLE I. MAGNITUDE OF INTERFERENCE DUE TO GLUCOSE

(A, unmodified Winkler procedure; B, permanganate modification)

PROCEDURE	GLUCOSE, P. P. M.:													
	0	10	20	40	80	120	160	200	400	600	1000	2000	5000	
	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	
INDICATED DISSOLVED OXYGEN CONTENT														
A	8.63	8.55	8.50	8.45	8.41	8.31	8.27	8.20	7.92	7.70	7.90	7.64	7.18	
B	8.64	8.57	8.55	8.55	8.43	8.45	8.42	8.30	8.20	8.00				
APPARENT LOSS OF DISSOLVED OXYGEN														
A	0.00	0.08	0.13	0.18	0.22	0.32	0.36	0.43	0.71	0.93				
B	0.00	0.07	0.09	0.09	0.21	0.19	0.22	0.34	0.44	0.64	0.74	1.00	1.46	

Finally, attention will be given to the determination of dissolved oxygen in chlorinated samples. The findings in this direction have a direct bearing on studies of chlorination as an adjunct to sewage treatment.

INTERFERENCE BY ORGANIC MATTER (GLUCOSE)

Experiments to test the extent of interference with the Winkler method by various forms of organic matter were undertaken, primarily, in connection with oxygen-demand studies in which a synthetic mixture containing glucose and peptone was being used. For the purposes of the present discussion these substances may also be regarded as typical of numerous forms of organic matter commonly found in waters polluted by sewage and industrial wastes.

minute period of contact, the test was completed in the usual manner.

As shown in Table I, the apparent loss of dissolved oxygen is progressively greater with increasing amounts of glucose, irrespective of the procedure used. With the unmodified or regular Winkler procedure, the loss of dissolved oxygen reaches 0.93 p. p. m. in the presence of 600 p. p. m. of glucose. Somewhat better results are obtainable with the permanganate modification, although it is clear that this procedure is only partly effective in counteracting the interference.

SOURCE OF INTERFERENCE

Numerous attempts were made to locate the source of the interference. Thus, on the theory that the apparent loss of

dissolved oxygen is due to absorption of iodine prior to the titration, the experiment was tried of adding varying amounts of acid for the final acidification. The regular Winkler procedure was used throughout. The results presented in Table II indicate that the amount of acid used is of little consequence. The behavior of glucose in this respect differs from that of the oxalates (15). These results also indicate that the period of standing after the final acidification and before titration is apparently not a factor.

TABLE II. EFFECT OF INCREASED ACIDITY ON INTERFERENCE DUE TO GLUCOSE

GLUCOSE P. p. m.	SULFURIC ACID (CONC.) ML.	TIME OF STANDING AFTER FINAL ACIDIFICATION Min.	INDICATED OXYGEN CONTENT P. p. m.	APPARENT LOSS ^a P. p. m.
0	1	15	8.56	0.04
0	2	16	8.63	-0.03
0	3	17	8.61	-0.01
0	4	18	8.60	0.00
200	1	5	8.06	0.54
200	2	6	8.24	0.36
200	3	7	8.21	0.39
200	4	8	8.19	0.41
200	1	23	8.24	0.36
200	2	24	8.27	0.33
200	3	25	8.14	0.46
200	4	26	8.21	0.39

^a Assuming that the correct oxygen content was 8.60 p. p. m.

In Table III results are presented which indicate that the apparent loss of dissolved oxygen from samples containing glucose does not depend on the amount of dissolved oxygen present. The dissolved oxygen in these experiments was varied by applying suction to partly filled carboys. Within the range of values found in natural waters, the apparent loss when the concentration of dissolved oxygen was relatively high was much the same as when water of low oxygen content was used.

TABLE III. EFFECT OF VARIATIONS IN DISSOLVED OXYGEN CONTENT ON INTERFERENCE DUE TO GLUCOSE

CONCENTRATION OF DISSOLVED OXYGEN	GLUCOSE, P. P. M.:		
	0 P. p. m.	40 P. p. m.	200 P. p. m.
INDICATED OXYGEN CONTENT			
High	7.80	7.72	7.46
Medium	6.72	6.57	6.06
Low	2.79	2.69	2.43
APPARENT LOSS			
High	0.00	0.08	0.34
Medium	0.00	0.15	0.66
Low	0.00	0.10	0.36

These preliminary experiments have indicated that interference by glucose probably occurs during the period of alkalization. Further experiments were therefore made to determine the influence of variations in pH value on the rate of oxidation of glucose. Consideration was also given to the effect of variations in pH value on the rate of absorption of dissolved oxygen by manganous hydroxide.

TABLE IV. RESULTS WITH CALCIUM HYDROXIDE AS ALKALINIZING AGENT

GLUCOSE P. p. m.	INDICATED OXYGEN CONTENT P. p. m.	APPARENT LOSS OF OXYGEN P. p. m.
0	7.73	(0.00)
10	7.67	0.06
20	7.69	0.04
40	7.73	0.00
80	7.70	0.03
120	7.60	0.13
160	7.57	0.16
200	7.55	0.18
400	7.43	0.30
600	7.23	0.50

In the experiments summarized in Table IV, a suspension of calcium hydroxide was used as an alkalizing agent in-

stead of the customary alkaline-iodide mixture. In this manner the pH value of the alkalized sample was reduced from the usual figure of 13 or over when the sodium hydroxide-potassium iodide mixture is used to a value of about pH 12. Acidification in the presence of the calcium hydroxide suspension was accomplished with hydrochloric acid, and a solution of potassium iodide was added as a separate reagent.

In comparison with results given in previous tables, it appears that the substitution of calcium hydroxide for sodium (or potassium) hydroxide does lead to somewhat better results when large amounts of glucose are present. The advantage, however, is not marked, and for the results given in Table IV it was only secured by extending the period of alkalization to fully 8 minutes. With shorter periods of contact, the results obtained were decidedly too low, even in the blanks, indicating that the rate of absorption of dissolved oxygen is greatly affected by any lowering of the pH value. As the decomposition of glucose proceeds at a measurable rate at pH 12, it must be concluded that any beneficial effect of working at this relatively low pH value is counteracted by the prolonged exposure required for the complete absorption of the dissolved oxygen.

TABLE V. RATE OF ABSORPTION OF DISSOLVED OXYGEN BY MANGANOUS HYDROXIDE

8 min. P. p. m.	PERIOD OF CONTACT WITH Mn(OH) ₂ :			
	1 min. P. p. m.	30 sec. P. p. m.	20 sec. P. p. m.	15 sec. P. p. m.
OBSERVED OXYGEN CONTENT ^a				
8.15	8.17	8.17	8.15	8.18
8.12	8.15	8.15	8.18	8.17
8.16	8.18	8.18	8.17	8.15
APPARENT LOSS OF OXYGEN ^b				
0.02	0.00	0.00	0.02	-0.01
0.05	0.02	0.02	-0.01	0.00
0.01	-0.01	-0.01	0.00	0.02

^a Triplicate determinations.
^b Basis of average value of 8.17.

RATE OF ABSORPTION OF DISSOLVED OXYGEN

On the basis of these and other experiments it appeared desirable to determine more closely the minimum time required for the complete absorption of dissolved oxygen by manganous hydroxide. In these experiments the medium was ordinary distilled water without addition of glucose. The usual Winkler reagents were used and the tests were started by the addition of 2 ml. of manganous sulfate solution followed by 2 ml. of alkaline-iodide reagent. The bottles were then stoppered and the precipitate was agitated, either continuously or at frequent intervals, so that the manganous hydroxide at all times was uniformly distributed throughout the bottle. To secure exact periods of contact, the sulfuric acid required for the final acidification was added before the precipitate had settled and a slight correction, the same in each case, was applied for the loss of the precipitate. Under these conditions, the reaction is practically complete in 15 seconds at ordinary temperatures (Table V) when intimate contact between the dissolved oxygen and the manganous hydroxide is maintained through the solution. Up to 8 minutes, the exact duration of the period of alkalization did not appear to be of consequence. It will be noted, however, that organic matter was absent in these experiments.

The technic in these experiments differed from that employed by Theriault (15) in similar experiments where the precipitate was allowed to settle completely each time before repeating the shaking. As the precipitate settles very readily, the actual period of contact with the upper portion of the liquid is uncertain when this procedure is followed, and complete absorption can only be obtained by repeating the shaking.

TABLE VI. EFFECT OF VARYING PERIODS OF ALKALINIZATION ON INTERFERENCE DUE TO GLUCOSE

PERIOD OF ALKALINIZATION	GLUCOSE, P. P. M.:										
	0	40	60	100	160	200	400	600	1000	2000	5000
	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
	APPARENT LOSS OF DISSOLVED OXYGEN ^a										
8 min.	(0.00)	0.10	0.14	0.14	0.14	0.30	0.58	0.74	1.02	1.52	2.45
4 min.	(0.00)	0.04	0.07	0.04	0.15	0.18	0.34	0.54	0.62	0.86	1.52
2 min.	(0.00)	0.00	0.07	0.04	0.08	0.06	0.14	0.24	0.40	0.51	0.92
25 sec.	(0.00)	0.00	0.02	0.00	0.00	0.02	0.05	0.10	0.13	0.20	0.36
15 sec.	(0.00)	0.00	0.00	0.10	0.02	0.09	0.05	0.10	0.13	0.24	0.26

^a Results with 1000 p. p. m. of glucose or over are averages of triplicate determinations.

IMPROVED TECHNIC FOR DISSOLVED-OXYGEN TESTS

Attempts were next made to reduce interference due to glucose by diminishing the period of contact with the alkaline-iodide to the minimum consistent with the complete absorption of dissolved oxygen. The effectiveness of this procedure in comparison with tests conducted over periods of alkalization of 2, 4, and 8 minutes is shown by the results presented in Table VI.

When the period of alkalization was 8 minutes, the precipitate was first uniformly distributed throughout the bottle and then allowed to settle completely before mixing for a second time. After a third mixing followed by complete subsidence of the precipitate, the sample was acidified and the liberated iodine was titrated with 0.025 *M* thiosulfate. A similar procedure was employed when the period of alkalization was 2 and 4 minutes, except that precipitates were allowed to settle only once and twice, respectively. The precipitate was continuously agitated when the shorter periods of 15 and 25 seconds were used and the acid was added before the precipitate had settled appreciably. The preliminary treatment with permanganate was not used.

The results presented in Table VI indicate that, in the presence of glucose and presumably other forms of organic matter, huge errors may be introduced in the Winkler method if the period of alkalization is prolonged beyond the time strictly necessary for the absorption of the dissolved oxygen. Under the given conditions, it seems fair to conclude that reasonably accurate results for dissolved oxygen can be obtained even in the presence of 5000 p. p. m. of glucose, provided the period of alkalization does not exceed 15 to 25 seconds. It would appear, therefore, that the absorption of dissolved oxygen by manganous hydroxide proceeds at a much faster rate than that of the interfering reaction due to the decomposition of glucose at high pH values. The apparent loss of dissolved oxygen when the period of alkalization is unduly prolonged may be ascribed to the reduction of the manganic hydroxide by the decomposition products of the glucose.

TABLE VII. MAGNITUDE OF INTERFERENCE DUE TO PEPTONE

(A, permanganate modification; B, regular Winkler procedure; C, abbreviated technic, 25 seconds contact; D, abbreviated technic, 15 seconds contact)

PROCEDURE	PEPTONE, P. P. M.:									
	0	20	40	80	120	160	200	400	600	1000
	P.p.m.	P.p.m.	P.p.m.	P.p.m.	P.p.m.	P.p.m.	P.p.m.	P.p.m.	P.p.m.	P.p.m.
	APPARENT LOSS OF OXYGEN									
A	(0.00)	0.20	0.27	0.44	0.57	0.94	1.41	..	2.12	2.85
B	(0.00)	0.10	0.05	0.11	0.15	0.19	0.32	0.62	0.74	1.43
C ^a	(0.00)	0.02	0.00	0.03	0.07	0.12	0.11	0.22	0.34	0.40
D	(0.00)	0.00	0.01	0.03	0.04	0.10	0.08	0.21	0.23	0.40

^a Average values in triplicate determinations. Other results are representative series of single observations.

It is to be noted that the rate of absorption of dissolved oxygen by manganous hydroxide depends not only on the pH value at which the reaction occurs but also on the amount of manganous hydroxide present in suspension. It can readily be shown that the period of alkalization should be approximately doubled when 1 ml. each of the Winkler reagents is used instead of 2-ml. portions as in the above experiments. A longer period of contact with manganous hydroxide must

also be allowed when phosphates, carbonates, and other buffering materials are present in large amounts. Clark (5) recommends a period of alkalization of at least 10 minutes when dissolved oxygen is determined in samples of sea water. With river waters and with ordinary domestic sewage, a period of contact of 20 to 25 seconds appears to be sufficient when 2-ml. portions of the Winkler reagents are added to 300-ml. samples.

INTERFERENCE BY PEPTONE

As shown in Table VII, the simple expedient of abbreviating the period of alkalization is also effective in reducing interference due to peptone. Using the regular Winkler procedure (2 ml. each of the reagents) and allowing the precipitate to settle twice, the apparent loss of dissolved oxygen was 0.74 p. p. m. when 600 p. p. m. of peptone (Difco) were present. The period of alkalization in this experiment was about 3 minutes. Using the modified technic (25 seconds' contact), this loss was reduced to 0.34 p. p. m. The corresponding loss with the permanganate modification was 2.12 p. p. m. With large amounts of peptone, the proposed technic is not so effective as with corresponding amounts of glucose. The improvement over the usual procedures is nevertheless marked.

As pointed out by Cooper, Cooper, and Heward (6) in work with peptone solutions, and as further shown by Theriault (15) for stale sewage, the results obtained with the permanganate modification are progressively lower as the period of contact with the permanganate solution is increased, the indication being that dissolved oxygen may be absorbed by peptone and by stale sewage even in the presence of permanganate. In the experiments presented in Table VII, this "immediate" demand effect was partly obviated by aerating the stock peptone solution prior to the test. Huge losses may be observed with freshly prepared peptone solutions and with stale sewage irrespective of the procedure used. For the purposes of oxygen-demand tests, the dissolved-oxygen content calculated from the known value for the dilution water may be more nearly correct than the value found by direct analysis. The error in question disappears when the samples are incubated under aerobic conditions for 24 hours or longer.

Apart from its usefulness in work with dilute solutions of dextrose or of peptone, the procedure of reducing the period of alkalization to a minimum has been found very effective in dealing with concentrated sewage mixtures and sludge liquors. The extension of this technic to such other forms of organic matter as may be encountered in various industrial wastes calls for special study of the individual waste. In dealing with sulfite wastes, for example, this modified or abbreviated technic appears very effective in repressing the deleterious effect of the organic matters present. It is of no value, however, in obviating interference due to the inorganic constituents (sulfites, polythionates, etc.) of such wastes.

INTERFERENCE BY SULFITE WASTES

A critical study of methods for the determination of dissolved oxygen in the presence of sulfite wastes was under-

taken in this laboratory in April, 1930, at the request of the State Department of Health of Maine, in preparation for a coöperative study of stream conditions. A report covering this survey has recently been published by a committee of paper manufacturers (Joseph A. Warren, chairman, Cumberland Mills, Maine) and the State Health Department (C. F. Kendall, commissioner, and E. W. Campbell, sanitary engineer) with the collaboration of C. L. Walker, Cornell University, and C. M. Baker, representing the American Pulp and Paper Association. Various modifications of the Winkler method were applied to samples of digester wastes furnished through the courtesy of representative paper manufacturers. The results obtained are of interest in elucidation of the mechanism of the interference. For this reason they will be briefly discussed before presenting the new modification which finally proved to be reasonably effective.

RIDEAL-STEWART MODIFICATION (PERMANGANATE)

Warrick (State Department of Health of Wisconsin; private communication) had previously indicated that the permanganate or Rideal-Stewart modification of the Winkler method is of doubtful value in counteracting interference due to sulfite wastes. Haase (8) has claimed that the permanganate treatment is useless with these wastes, and in a later publication (9) he has proposed an empirically calibrated electrochemical procedure for the determination of dissolved oxygen in the presence of sulfites.

Bach (2) has confirmed the findings of Haase in regard to the deficiencies of the permanganate procedure and has shown that sodium sulfite may be present in amounts up to 1000 p. p. m. when the Miller (ferrous ammonium tartrate and safranin) procedure is used provided that alcohol, at the rate of 10 ml. of 95 per cent ethyl alcohol per liter, is added as a preliminary treatment.

There is ample evidence in the literature (10) that the oxidation of sulfites by permanganates and also by bromates does not proceed to completion. It appears probable that dithionic acid is formed along with sulfate, so that only 90 to 95 per cent of the total sulfite is actually oxidized to sulfate. It is not surprising, therefore, that the Rideal-Stewart (permanganate) modification should prove inadequate in the presence of relatively large amounts of sulfite wastes.

Experiments with the permanganate modification indicate that, in water containing 8 or 9 p. p. m. of dissolved oxygen, the results obtained after adding 1 volume of digester waste to 1000 volumes of water may be 3 or 4 p. p. m. too low. The total absence of dissolved oxygen may be indicated at dilutions of 1 to 300. As shown by direct observations on the rate of absorption of dissolved oxygen by sulfite wastes, this loss is only apparent. It is not difficult, for instance, to produce a laboratory condition where fish are swimming freely in a water apparently devoid of dissolved oxygen on the basis of the permanganate modification.

ALSTERBERG MODIFICATION (BROMINE)

The Alsterberg (1) modification, based on a preliminary treatment with bromine with subsequent removal of the excess of reagent by salicylic acid, gave somewhat better results than the permanganate treatment. At best, however, the errors were still too great to make this modification of any value for the purpose at hand. The period of contact with the bromine was only 2 minutes in these experiments. A 24-hour period of contact, as recommended by Alsterberg, is impractical with sulfite wastes.

NOLL MODIFICATION (IODINE)

The preliminary oxidation of interfering substances has been accomplished by Noll (13) through the use of iodide

in the presence of manganic salts. A solution of iodine is recommended by Lunge (11) and by Winkler (18) when organic matter is present. It is now well known that the oxidation of sulfites by iodine proceeds to completion with the formation of sulfates. This modification, therefore, appeared promising in dealing with sulfite wastes.

In applying the iodine modification, a solution of potassium biniodate was first added to 300-ml. sample bottles filled with distilled water to which graded amounts of a freshly prepared stock solution of sodium sulfite had also been added. Iodine was then released by acidification in the presence of an iodide. After standing for a few minutes, 0.2 ml. of starch solution was added to serve as an indicator and the excess of iodine was removed by the addition of thiosulfate solution, thereby forming tetrathionates. Dissolved oxygen was then determined by the regular Winkler procedure, starting with the addition of 2-ml. portions of manganous sulfate and of alkaline-iodide solutions. Starch solution, in the amount added, does not interfere with the Winkler method.

It was noted that the brown precipitate of manganic hydroxide which first forms became rapidly lighter in color on standing. The results for dissolved oxygen were decidedly low, the error increasing somewhat in proportion to the amount of thiosulfate used in the preliminary treatment. Chapin (4) has clearly shown that "tetrathionates are notably sensitive to even low concentrations of hydroxyl ions, although only slightly affected by sodium bicarbonate." The decomposition leads to the formation of sulfites and thiosulfates by which the manganic hydroxide can be reduced to the manganous condition (12). With particular reference to the determination of arsenic, but with equal application to the present problem, Chapin (4) recommends that "as a discharging agent for iodine. . . . it seems safer to abandon the use of thiosulfate altogether, and to substitute therefor a dilute solution of sodium sulfite."

Avoiding the use of thiosulfate for the removal of iodine, the preliminary oxidation of sulfites was next accomplished by the cautious addition of an iodine solution to an end point, again using starch as an inside indicator. In other experiments a definite excess of iodine was added and the decolorization was accomplished with a dilute solution of sodium sulfite. Accurate results were obtained in either case with sulfites present to the extent of 2.0 to 12.0 ml. of 0.025 *M* sodium sulfite in 300 ml. of distilled water. The loss of dissolved oxygen from dilute sulfite solutions was negligibly small over the short period of standing required in these experiments. In time, however, a gradual deoxygenation is readily shown.

The observation, that the use of thiosulfates for the removal of iodine prior to the addition of the Winkler reagents is unsound, has an obvious bearing on studies of the chlorination or superchlorination of sewage, industrial wastes, and grossly polluted waters. The usual procedure has been to discharge the excess of chlorine by the addition of an iodide. The liberated iodine is then removed with thiosulfate. The dechlorinated sample may then be used for dissolved-oxygen or oxygen-demand tests. In cases where an excess of iodine is necessarily present, it is obviously advisable to substitute sulfites for thiosulfates in the removal of free iodine, thereby forming stable sulfates instead of the readily decomposable tetrathionates.

Although a preliminary treatment with iodine is very efficacious in obviating interference due to sulfites, this procedure was found to be of little value in dealing with sulfite wastes. The indications are that sulfites, as such, are of minor significance in these waste liquors. Other modifications of the Winkler method were therefore examined.

MANGANOUS CARBONATE MODIFICATION

Winkler (18) has proposed an ingenious modification of his original procedure for dissolved oxygen for use in the presence of nitrites and organic matter. The test is conducted in the usual manner up to the removal of dissolved oxygen by the formation of manganous hydroxide, except that the alkalizing solution need not contain any iodide. The excess of manganous hydroxide is then converted to carbonate by leading in carbon dioxide or by the addition of solid sodium acid carbonate (3). As the carbonate does not absorb oxygen from air, interfering substances are then removed by filtration and the test is completed on the precipitate itself.

In blank experiments using sodium acid carbonate it was found that high results were obtained when the hydrogen-ion concentration corresponded to pH 10 or thereabouts. The best results were obtained by adjustment of solution in the range of pH 7 to 8 with phosphoric acid. At still lower pH values, low results were obtained owing to the loss of precipitate by resolution.

In work with pure sulfite solutions, low results were invariably obtained, irrespective of pH adjustments. As already shown, this loss is due to the reduction of the manganic hydroxide by the sulfite, so that the subsequent filtration is purposeless.

Applied to sulfite wastes, the method gave somewhat better results than previously described procedures. At best, however, the errors were still much too great to warrant the extension of this modification to the paper-mill wastes.

MANGANIC CHLORIDE MODIFICATION

The reduction of the manganic hydroxide formed in the course of the dissolved-oxygen test suggests the possibility of counteracting this interference by a preliminary treatment with manganic salts, as originally proposed by Winkler (17). A precipitate of manganous hydroxide was accordingly oxidized by air, and, after acidification, the resulting suspension was used as an oxidizing agent. The excess of manganic salt was reduced by adding potassium iodide, and the liberated iodine was in turn removed with sodium sulfite. The results obtained in this double treatment with manganic salts and iodine were unsatisfactory and the procedure was abandoned.

ACID HYPOCHLORITE MODIFICATION

Winkler (19) has proposed a fourth modification of his original procedure for the determination of dissolved oxygen, based on a preliminary treatment of samples containing readily oxidizable substances with calcium hypochlorite in acid solution. The excess of reagent is removed with potassium thiocyanate and a correction is applied by running a blank.

This method and a later revision (20) proved impractical in work with sulfite wastes owing to the difficulty of obtaining accurate values for the blanks. The results obtained were nevertheless encouraging.

ALKALINE-HYPOCHLORITE MODIFICATION

On the basis of the foregoing experiments and in accord with the work of Foerster et al. (7) on the equilibrium between sulfurous acid and its salts in aqueous solution, the conclusion seems warranted that the interference of sulfite wastes with the Winkler method is only partly due to sulfites as such. As shown by direct titration with iodine solutions, the amount of sulfite present in these wastes is relatively small. The iodine-consuming capacity of these wastes may be increased thirty fold, however, upon treatment with hydroxides. It is probably to the readily decomposable

polythionates and to similar organic sulfur compounds that interference due to sulfite wastes is to be ascribed. Under the highly alkaline conditions of the Winkler procedure, it is to be expected that these sulfur compounds would break down to form sulfites and thiosulfates. It is obvious that interference would then occur either by reduction of manganic hydroxide or by removal of iodine, as in the final step of the Winkler process.

A preliminary treatment of the sulfite wastes with alkalis, followed by a treatment with iodine in acid solution, does not remedy the situation, as the oxidation of the thiosulfates and trithionates only proceeds to the formation of tetrathionates which are later broken down during the subsequent period of alkalization.

Now it is known that the oxidation of thiosulfates and the higher polythionates does proceed to completion under the action of chlorine. The method finally adopted, therefore, for the determination of dissolved oxygen in the presence of sulfite wastes consists in a preliminary treatment of the sample with a highly alkaline solution of a hypochlorite. As these conditions are also favorable to the reaction of dissolved oxygen with organic matter and with inorganic sulfur compounds, this preliminary treatment must necessarily be brief. The subsequent treatment calls for the removal of the undecomposed hypochlorite. This is accomplished by acidifying the sample in the presence of an iodide, which is in turn removed with a dilute solution of sodium sulfite. Dissolved oxygen may then be determined in a solution supposedly freed from sulfites, thiosulfates, and the polythionates, although notable amounts of relatively stable forms of organic matter are still present. The technic developed in the first part of this paper for use in the presence of such forms of organic matter as glucose also appears to be reasonably effective in dealing with the organic components of sulfite wastes.

The reader is referred to Supplement No. 90 to *Public Health Reports* (16) for detailed instructions regarding the performance of the dissolved-oxygen test in the presence of various interfering substances. For sulfite wastes the recommended procedure is substantially as follows:

1. Add enough alkaline-hypochlorite reagent (1 *M* sodium hypochlorite in 0.1 *M* sodium hydroxide) to oxidize the sample, avoiding a great excess.

With river water polluted with sulfite wastes, 0.2 ml. of the alkaline-hypochlorite reagent may be added as a trial amount. In oxygen-demand work, add 1 ml. of alkaline-hypochlorite reagent for each milliliter of digester waste present in the bottle under examination.

The alkaline-hypochlorite reagent may be prepared by passing chlorine gas through 2.1 *M* sodium hydroxide, with cooling, until a 1-ml. test portion of the chlorinated solution requires about 20 ml. of 0.10 *M* thiosulfate for the neutralization of the iodine released upon acidification in the presence of an iodide. This reagent should give more than a fleeting color with phenolphthalein.

2. Mix well by inverting rapidly a few times. The duration of this treatment should not greatly exceed 20 seconds.

3. Acidify the sample by adding 1 ml. of dilute sulfuric acid (10 per cent solution) and add 1 ml. of 1 *M* potassium (or sodium) iodide to release iodine. Shake.

4. Neutralize the liberated iodine with 0.1 or 0.025 *M* sodium sulfite, using 0.2 ml. of starch solution as an inside indicator. If the end point is greatly overstepped, it may be restored with 0.1-ml. portions of 0.1 or 0.025 *M* potassium biniodate or iodate.

The reaction between sulfites and iodine to form sulfates is complete, under the given conditions, only in very dilute solution. Relatively low results will be obtained when more than 3 ml. of 0.05 *M* (0.1 *N*) sulfite are required for the neutralization of the iodine. On the other hand, if only 0.1 ml. or thereabouts of 0.05 *M* sulfite is required, it may be assumed that an insufficient amount of alkaline-hypochlorite has been used.

5. Add 1 ml. of the usual manganous sulfate solution and 1.3 ml. of alkaline-iodine solution. A slight excess (0.3 ml.) of the alkaline-iodine solution is used in order to neutralize the acid added during the preliminary treatment. The period of

TABLE VIII. MAGNITUDE OF INTERFERENCE DUE TO SULFITE WASTES

(A, permanganate modification; B, regular Winkler procedure; C, alkaline-hypochlorite modification)

METHOD	DILUTION OF DIGESTER WASTE												
	1 to 300,000	1 to 150,000	1 to 60,000	1 to 30,000	1 to 15,000	1 to 10,000	1 to 6000	1 to 3000	1 to 1500	1 to 1000	1 to 600	1 to 300	1 to 150
	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
	APPARENT LOSS OF OXYGEN ^a												
A	-0.06	0.00	-0.06	0.12	0.34	0.45	0.77	1.68	2.78	3.58	5.67	8.27 ^b	..
B	0.03	0.07	0.10	0.15	0.02	0.30	0.24	0.54	1.17	1.74	2.63	4.59	7.22
C	0.00	0.05	0.02	0.00	0.04	0.07	0.06	-0.06	0.10	0.16	0.20	0.30	1.10

^a Average values in triplicate determinations.^b Corresponding to the total absence of dissolved oxygen.

contact with the manganous hydroxide should not exceed 40 to 50 seconds.

6. The titration should not be delayed, as a measurable loss of iodine occurs on standing.

Comparative results with the permanganate modification (A), with the unmodified Winkler procedure (B), and with the alkaline-hypochlorite modification (C) are given in Table VIII. Satisfactory results are obtained by all three procedures when the concentration of digester waste does not exceed 1 part in 30,000 of water. The results with the permanganate modification are decidedly low at dilutions of 1 to 10,000, and the complete absence of dissolved oxygen may be indicated by this procedure at dilutions of 1 to 300.

On the whole, the unmodified or regular Winkler method gives better results with sulfite wastes than the permanganate modification. Huge errors, nevertheless, are introduced at dilutions of 1 to 3000 or less.

The alkaline-hypochlorite modification gives reasonably accurate results even in the presence of 1 part of digester waste in 300 parts of sample, corresponding to the situation which might be encountered at sampling points in the immediate vicinity of a paper mill. At dilutions of 1 to 150, however, this method also shows signs of failure.

It will be noted that the values given in Table VIII refer to the apparent loss of dissolved oxygen and not to the dissolved-oxygen content. The actual dissolved-oxygen content in all cases was in the neighborhood of 8.5 p. p. m. prior to the addition of digester waste. The possibility exists that, under rigid conditions of test, these apparent losses with different procedures might serve as an index to the

amount of waste present in a sample of river water. A less cumbersome and more sensitive test might be devised on the basis of the increase in iodine-consuming capacity of a sample following a treatment with hydroxides.

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Volumetric Determination of Chloride

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DENIGÈS determined silver in a large number of compounds by adding excess standard potassium cyanide to an ammoniacal solution of the silver salt, and by titrating the excess cyanide with silver nitrate, using potassium iodide as indicator (1). Substances such as silver iodide, which are insoluble in ammonium hydroxide, were brought into solution by the addition of excess standard potassium cyanide to the ammoniacal solution. Silver salts insoluble in potassium cyanide, such as silver sulfide, were dissolved in nitric acid. The solution was then made ammoniacal and the silver was determined as above.

Chloride, bromide, and iodide each were determined by precipitation with excess standard silver nitrate, filtration, and determination of the silver as above in an aliquot of the filtrate. Lestra (2) separated chloride, bromide, and iodide by means of the difference in the solubility of their silver salts in ammonium hydroxide, and determined all by a combination of the Mohr method and the method of Denigès.

Since the method of Denigès (1) affords a convenient way to determine silver and many anions by use of only two stand-

ard solutions, a study was made of the method to see if the procedure could be modified slightly to make it more accurate and more convenient to carry out.

EFFECT OF VOLUME, AMMONIUM HYDROXIDE CONCENTRATION, AND INDICATOR CONCENTRATION

Denigès carried out titrations in from about 125 to 250 cc. of solution, containing 10 drops of *N* potassium iodide, and from about 0.2 to 0.6 *N* in ammonium hydroxide. In determining iodide in the presence of bromide, Lestra carried out titrations in about 6 *N* ammonium hydroxide. It takes 1.6 cc. more of 0.1 *N* silver nitrate to react with 24 cc. of 0.1 *N* potassium cyanide in 250 cc. of 6 *N* ammonium hydroxide than it does in 125 cc. of the same strength ammonium hydroxide, with 10 drops of potassium iodide as indicator, in each case. In 3 *N* ammonium hydroxide, with the same amounts of indicator and potassium cyanide as above, it takes over 0.9 cc. more of silver nitrate in 250 cc. of solution than it does in 125 cc. (In the absence of potassium cyanide, 0.02 cc. of 0.1 *N* silver nitrate causes a distinct turbidity in 250 cc. of 3 *N*

ammonium hydroxide, containing 10 drops of *N* potassium iodide.) Even in 0.6 *N* ammonium hydroxide, with 10 drops of *N* potassium iodide as indicator (conditions used by Denigès in some titrations), changing from 125 to 250 cc. causes a change of 0.16 cc. in the end point when titrating 24 cc. of cyanide. Thus, it is evident that if 0.6 *N* or more concentrated ammonium hydroxide is to be used, with 10 drops of iodide as indicator, accurate results can be obtained only by carrying out standardization and analyses under almost identical conditions.

Increase in potassium iodide concentration causes the effect of volume change to be lessened. The best results were obtained by using an amount of indicator proportional to the volume of the solution, and by carrying out titrations in fairly weak ammoniacal solutions. A satisfactory concentration of indicator was found to be 1 cc. of *N* potassium iodide for 50 cc. of solution. With this concentration, decrease in ammonium hydroxide concentration from 0.25 to 0.1 *N* has little effect on the end point. Also, in 0.25 *N* ammonium hydroxide, the effect of volume of solution on the end point is very slight. It is not convenient, frequently, to use a weaker concentration of ammonium hydroxide than this, so subsequent titrations were carried out in 0.25 *N* ammonium hydroxide, containing 1 cc. of *N* potassium iodide for each 50 cc. of solution.

TEST OF METHOD

Denigès showed that cyanide titration of silver ions can be used advantageously to determine all types of silver compounds and anions which form insoluble silver salts. Since in all cases the reaction is between silver ion and cyanide, with iodide as indicator, the conclusions reached above as to the most desirable ammonium hydroxide and potassium iodide concentrations should apply to all the determinations Denigès made.

For an analytical method to be of greatest value it should give consistent and accurate results over a wide range of concentrations of the substance being determined. Since silver nitrate can be readily and accurately standardized, it was chosen as a source of silver to test the method of Denigès. The silver nitrate solution was standardized gravimetrically as silver chloride and the potassium cyanide solution was standardized by comparison with the silver nitrate. In samples of silver nitrate containing from 0.0504 to 0.4882 gram of silver, the maximum error was 0.3 mg. and the average error 0.15 mg. of silver. Thus, it is evident that the slightly modified method of Denigès should give fairly accurate results for all soluble silver salts, when no interfering ion or substance is present.

A solution of hydrochloric acid, approximately 0.05 *N*, was standardized gravimetrically, and was used as a source of chloride in testing the method. Since the method varies slightly in detail from that of Denigès, the procedure is given, as follows:

Precipitate the chloride with silver nitrate solution containing nitric acid and wash free of acid-soluble silver salts, largely by decantation. Dissolve the precipitated silver chloride on the filter paper with dilute ammonium hydroxide, catching the filtrate in the beaker containing the bulk of the precipitate. If more concentrated than 0.25 *N* ammonium hydroxide is used, dilute to approximately this strength. (Do not partially neutralize to cut down the ammonia strength for, in the presence of a high concentration of a strong electrolyte, silver iodide has a tendency to coagulate, and the end point is determined with difficulty. Some of Denigès' work was done in the presence of appreciable concentrations of strong electrolytes.) If all the silver chloride does not dissolve readily in the ammonium hydroxide, start titrating with cyanide, using a policeman to crush the particles of silver chloride to bring them into intimate contact with the solution. When the chloride is in solution, add a drop or two of indicator. (If iodide is added before the

precipitate is completely dissolved, coagulated silver iodide is formed, and this dissolves slowly in potassium cyanide. Under the experimental conditions outlined in this procedure, the titration is carried out in a solution which has a low concentration of strong electrolyte. Under such conditions, the formed silver iodide does not coagulate, but remains in a very finely divided, readily soluble form.) If a precipitate is obtained, continue titration with cyanide to its disappearance before adding the remainder of the indicator, 1 cc. of *N* potassium iodide for each 50 cc. of solution. Titrate till a very faint turbidity persists, using standard silver nitrate to back titrate, if necessary.

By the above procedure, chloride was determined in volumes of the hydrochloric acid solution varying from 2.49 to 100.00 cc. The error varied from 0.0 to 0.2 mg. (average, 0.07 mg.) with weights of chloride from 0.0045 to 0.1800 gram.

The same procedure with slight modifications was used to determine chloride in the presence of various substances which normally interfere with either the Volhard or Mohr method, or both (see Table I).

TABLE I. DETERMINATION OF CHLORIDE IN HYDROCHLORIC ACID, IN PRESENCE OF OTHER SUBSTANCES

(Chloride present, 0.0899 gram)		
SUBSTANCE PRESENT		CHLORIDE FOUND
Name	Amount Gram	
Co ⁺⁺ , Cu ⁺⁺ , Ni ⁺⁺	0.5 each	0.0899
Fe(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O; FeNH ₄ (SO ₄) ₂ ·12H ₂ O	1.0 each	0.0897
K ₂ Cr ₂ O ₇	1.0	0.0899
KMnO ₄	1.0	0.0899
Pb ⁺⁺ , Bi ⁺⁺⁺	1.0 each	0.0900
Na ₂ HPO ₄ ·H ₂ O	1.0	0.0898
KI	2 cc. <i>N</i>	0.0896
KNO ₃	1.0	0.0898
Gallic acid	1.0	0.0899
Fe(CN) ₆ ⁴⁻	0.20	0.0886

It was necessary to neutralize the hydrochloric acid before the permanganate and nitrite were added. After the addition of the silver nitrate, these two solutions were acidified with nitric acid. It was necessary to make the solution more strongly acidic than is usually the case, to hold silver chromate in solution. In the samples containing permanganate and bichromate, the precipitates of silver chloride were washed with sulfurous acid to remove impurities. Ferricyanide was reduced to ferrocyanide by sodium sulfite, in ammoniacal solution. Reduction of ferricyanide was not likely complete, for a similar test with ferricyanide alone yielded a slight amount of ammonia-soluble silver ferricyanide. Since the precipitate of silver ferrocyanide had a tendency to become colloidal in ammoniacal solution, the ammonium hydroxide washings of silver ferrocyanide were not added to the main filtrate. No doubt some chloride was left in the precipitate and the result obtained represents a balancing of errors. The method as outlined, therefore, is not to be recommended for accurate determination of chloride in the presence of ferricyanide.

Chloride was separated from iodide and the formed ferrocyanide by the solubility of silver chloride in approximately *N* ammonium hydroxide, and the silver chloride was precipitated by the addition of nitric acid to the ammoniacal solution.

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Effect of Temperature on Determination of Water-Soluble Matter in Leather

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IN DETERMINING water-soluble matter in vegetable-tanned leather by Wilson's method (2), a weighed sample of leather is first freed from fat by extraction with chloroform, and then extracted with running distilled water in a Wilson-Kern extractor until the percolate no longer gives a positive test for non-tannin with ferric chloride. For calf upper leather, with a water flow of approximately 500 cc. per hour, this point is generally reached in 4 days. When the percolate no longer gives a positive test with ferric chloride, the leather is removed quantitatively from the extractor, dried first at 50° C. and then at 102° C., and weighed. The difference between 100 per cent and the sum of the percentages of water and fat (in the original leather) and water-insoluble residue is taken as percentage of water-soluble matter.

In the author's laboratory, the determination is carried out at room temperature. The question arises as to how great is the effect of seasonal differences in laboratory temperature upon the rate of extraction of water-soluble matter from the leather. To settle this point, samples of hide powder

Chemists' Association method). After 24 hours the powder was filtered on a muslin cloth, wrung out by hand, and placed in a fresh 2000-cc. portion of liquor. This process was repeated five times. Finally the tanned powder was freed from adhering tan liquor by alternately suspending it in distilled water and wringing out, until the washings were practically colorless. The powder was then air-dried, and analyzed for water, ash, and hide substance. Tannin plus water-soluble matter was obtained by difference.

PROCEDURE

Fifty grams of air-dry tanned hide powder were placed in each of four modified Wilson-Kern extractors (1) which were immersed to the necks in thermostats at 10°, 20°, 30°, and 40° C., respectively. The ground-glass joints were protected against possible leakage by a section of tightly fitting Gooch filter tubing. The outlet of each extractor was attached to a capillary tube bent into an inverted U, which served to carry the percolate over the thermostat wall. The inlet of each extractor was attached to a reservoir of distilled water. The distilled water level inside the extractors was such as to submerge completely the charge at all times. The rate of flow of the distilled water was adjusted to 500 cc. per hour.

At the end of 1, 2, 4, 8, 16, and 32 days, each extractor was removed from its thermostat, and an amount of wet hide powder was withdrawn equivalent to about 7 grams in the air-dry state. Each portion withdrawn was composed of equal weights taken from the top and from the bottom of the hide-powder column in the extractor. Each portion was air-dried, and analyzed for water, ash, and hide substance. Apparent percentage of tannin was obtained by difference for each temperature and period of washing. The percentage of water-soluble matter—i. e., per cent of the original tanned powder that had dissolved—was calculated by finding the number of grams of vegetable matter, after washing, which was combined with a number of grams of hide substance equal to the per cent of hide substance in the original leather, and subtracting this number from the percentage of tannin plus water-soluble matter in the original leather. All percentages were corrected to the water-free basis.

RESULTS

The percentage of water-soluble matter found in this manner for extraction periods of 1 to 32 days, at temperatures of 10° to 40° C., are given in Table I and in Figure 1. The rate of extraction, as shown in Figure 1, increases markedly from 10° to 20° C., but is little affected by further increase in temperature. For a 4-day extraction period, the percentage of water-soluble matter found increases 0.43 per cent per degree rise in temperature between 10° and 20° C., but only 0.09 per cent per degree between 20° and 30° C., and only 0.07 per cent per degree between 30° and 40° C. Thus an increase in temperature from 20° to 30° would increase by only 0.9 per cent the percentage of water-soluble matter found by a 4-day extraction at room temperature. Agreement of duplicate determinations to within 1 per cent is considered passable in this laboratory, so that we may conclude that only in the most extreme hot weather will high room temperatures materially affect the analytical results. On the other hand, it is very evident that, if the temperature is al-

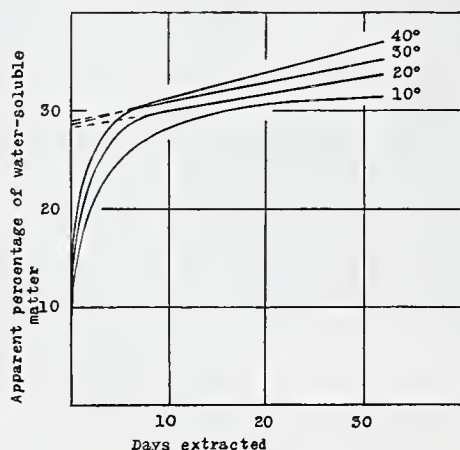


FIGURE 1. RATE OF EXTRACTION OF WATER-SOLUBLE MATTER FROM OAK-BARK-TANNED HIDE POWDER AT DIFFERENT TEMPERATURES

tanned with oak-bark extract were extracted at temperatures of 10°, 20°, 30°, and 40° C. for periods of from 1 to 32 days. Results show that increasing the temperature from 20° to 40° C. has very little effect upon the rate of extraction of water-soluble matter from leather, and that a change from 20° to 30° (the usual laboratory range) produces an effect which is less than the difference frequently found between duplicate determinations run side by side. A change in temperature from 20° to 10° C., however, markedly retards the extraction of water-soluble matter. It is concluded that control of temperature is unnecessary in determining water-soluble matter by Wilson's method, except that the temperature of the room must not be less than 20° C. If this condition cannot be fulfilled, the distilled water used should be preheated to 25° C., say by passing it through a block tin coil in a bath maintained at 25° ± 1° C.

MATERIALS

Two hundred grams of purified hide powder (3) were suspended in 2000 cc. of a solution containing 80 grams of liquid oak-bark extract (1 per cent tannin by the American Leather

owed to fall even a few degrees below 20° C. and the time of extraction is kept at 4 days, the results obtained will be abnormally low. When a minimum room temperature of 20° C. cannot be maintained day and night during the extraction of water-soluble matter, it appears advisable to bring the infowing water to 25° C., which can be done very simply by passing it through a block tin coil in a bath maintained at the desired temperature within a range of $\pm 1^{\circ}$.

TABLE I. EFFECT OF TEMPERATURE UPON RATE OF EXTRACTION OF WATER-SOLUBLE MATTER FROM OAK-BARK-TANNED HIDE POWDER

DAYS WASHED	APPARENT WATER-SOLUBLE MATTER FOUND AT:				INCREASE PER DEGREE IN TEMPERATURE INTERVAL AT:		
	10° C.	20° C.	30° C.	40° C.	10-20° C.	20-30° C.	30-40° C.
	%	%	%	%	%	%	%
1	16.8	18.9	20.8	21.8	0.21	0.19	0.10
2	19.8	23.0	(22.6)	24.5	0.32	(-0.04)	0.19
4	22.7	27.0	27.9	28.6	0.43	0.09	0.07
8	27.1	29.6	30.4	30.6	0.25	0.08	0.02
16	30.0	30.9	32.0	32.7	0.09	0.11	0.07
32	31.4	33.6	35.1	37.0	0.22	0.15	0.19

The shape of the several extraction curves is interesting in that these curves do not converge, but rather tend to become

straight lines whose slopes increase with increasing temperature. It appears reasonable to suppose that the slope of the rectilinear portion of each curve represents the rate of hydrolysis of the hide-tannin compound at the temperature in question. If this be true, then by extrapolating to zero time the rectilinear portion of each curve, a value would be obtained which would represent the percentage of water-soluble matter in the leather corrected for dissolved tannin. When this is done, for the four curves of Figure 1 the corrected values for water-soluble matter show an extreme variation of less than 0.5 per cent, indicating that the distinction between fixed tannin and water-soluble matter is not affected by change in temperature of extraction over the range studied.

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RECEIVED July 8, 1931. Presented before the Division of Leather and Gelatin Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8 to 12, 1930.

Binary System Carbon Tetrachloride-Ethylene Dichloride

Their Boiling Points and Specific Gravities as Aids in Analysis

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SINCE carbon tetrachloride-ethylene dichloride mixtures have been used as fumigants against moths and other insects (1), it has become increasingly important to find a rapid and reliable method of ascertaining the ratio of the two components in such a mixture. Carbon tetrachloride contains 92.20 per cent chlorine and ethylene dichloride 70.65 per cent, the difference being 21.55 per cent. To detect a difference of 1 mole per cent in the composition of a mixture of these compounds by a determination of the chlorine content would therefore require that this constituent be known to the nearest 0.2 per cent. Such a degree of accuracy might possibly be attainable by the best methods now in use, but only by taking extreme precautions with consequent loss of time.

ANALYSIS BY PHYSICAL METHODS

Three physical constants—refractive index, specific gravity, and boiling point—were considered as offering bases upon which to found a method of analysis. Rosanoff and Easley (2) found the refractive indices of carbon tetrachloride and ethylene dichloride at 25.2° C. to be 1.45730 and 1.44218, respectively. As these figures are so close together that extreme care under very closely controlled conditions would be necessary to get any results at all, nothing further was done with this factor. The specific gravities determined on purified samples prepared by prolonged drying of chemically pure reagent materials over calcium chloride followed by distillation, were found to be 1.591 for carbon tetrachloride and 1.252 for ethylene dichloride, both at 20° C. This is a more favorable difference, and the whole composition-specific gravity relationship was therefore determined.

The pure compounds were mixed in the following ratios (mole per cent): 100% CCl₄; 90% CCl₄ and 10% C₂H₄Cl₂; 80% CCl₄ and 20% C₂H₄Cl₂; . . . 0% CCl₄ and 100% C₂H₄Cl₂. The observed specific gravities of these mixtures are given in Table I and shown graphically in Figure 1. As would be expected, the specific gravity-composition curve shows no irregularities, so a determination of this constant alone might be used to ascertain the composition. The total range of specific gravity is about 0.340, equivalent to approximately 0.0034 per 1 mole per cent change in the concentration of one of the constituents. Therefore, specific-gravity determinations can be made to yield analyses with an accuracy of ± 1 mole per cent, always with the assumption, of course, that the mixture contains no impurity.

TABLE I. SPECIFIC GRAVITIES AND BOILING POINTS OF CARBON TETRACHLORIDE, ETHYLENE DICHLORIDE, AND MIXTURES OF THE TWO

COMPOSITION IN MOLES		SPECIFIC GRAVITY AT 20°/20°	BOILING POINT AT 760 MM. ° C.
CCl ₄	C ₂ H ₄ Cl ₂		
%	%		
100	0	1.591	76.52
90	10	1.563	75.82
80	20	1.531	75.42
70	30	1.500	75.30
60	40	1.469	75.39
50	50	1.435	75.74
40	60	1.402	76.39
30	70	1.367	77.26
20	80	1.330	78.49
10	90	1.292	80.23
0	100	1.252	82.85

The difference in boiling points between ethylene dichloride and carbon tetrachloride is 6.33° C. As boiling-point differences can be determined to about $\pm 0.002^{\circ}$ (the limit of accuracy of a Beckman thermometer), it is evident that very

small changes in concentration might be detected by boiling-point determination in this system. For this purpose it was necessary to establish the entire composition-boiling point relationship in the system, since, so far as could be found by examining the literature, this had not been done previously.

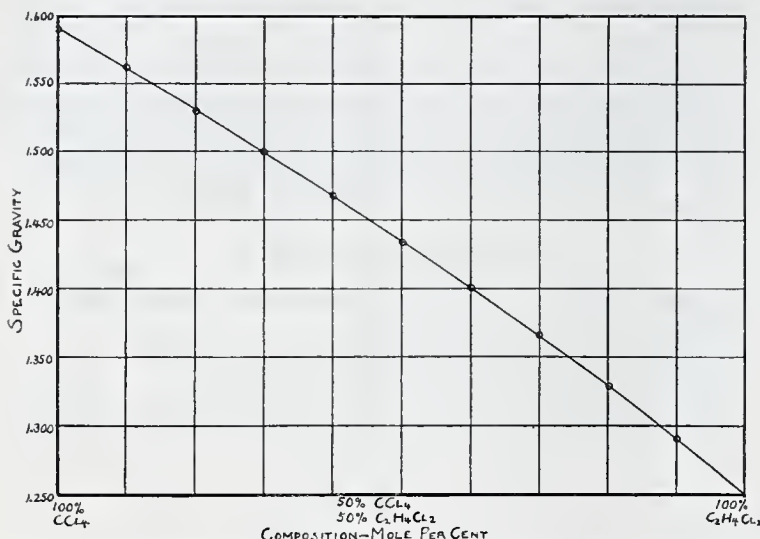


FIGURE 1. SPECIFIC GRAVITIES OF MIXTURES OF PURE COMPOUNDS

The apparatus used for determination of boiling points was that developed by Swietoslawski (4). It is claimed for this apparatus that "it is easy to detect the difference in the boiling temperature caused by removing the apparatus from the level of the laboratory table to that of the floor."

All boiling-point determinations were made at atmospheric pressure, and were calculated to 760 mm. by Landolt's equation $dT/dP = 0.043^\circ/\text{mm}$. The accuracy of this equation was confirmed experimentally by observing the boiling points of both compounds, as well as of several of the mixtures, at different pressures.

The results are given in Table I, and are represented graphically by the lower curve in Figure 2.

TABLE II. COMPOSITION OF DISTILLATES FROM VARIOUS CARBON TETRACHLORIDE-ETHYLENE DICHLORIDE MIXTURES

B. P. OF SOLN. AT 760 MM. ° C.	COMPOSITION OF SOLN. IN MOLES		B. P. OF DISTILLATE AT 760 MM. ° C.	COMPOSITION OF DISTILLATE IN MOLES	
	CCl ₄ %	C ₂ H ₄ Cl ₂ %		CCl ₄ %	C ₂ H ₄ Cl ₂ %
76.20	96.0	4.0	75.86	90.7	9.3
75.95	92.3	7.7	75.68	87.5	12.5
75.86	90.0	9.1	75.56	84.8	15.2
75.71	88.0	12.0	75.50	83.1	16.9
75.78	50.6	49.4	75.53	55.7	44.3
76.62	37.0	63.0	75.93	47.3	52.7
78.73	18.5	81.5	77.23	31.0	69.0
80.27	9.7	90.3	78.53	20.2	79.8
80.39	9.1	90.9	78.61	18.5	81.5
81.59	4.0	96.0	79.81	14.1	85.9

The composition-boiling point data show that there is a minimum boiling point of 75.30°C . at a concentration of approximately 70 mole per cent of carbon tetrachloride. The data show also that from 100 per cent ethylene dichloride to 40 mole per cent carbon tetrachloride–60 mole per cent ethylene dichloride, the composition can be determined to an accuracy of better than 0.10 per cent by reading the thermometer to 0.01°C ., but from 100 per cent carbon tetrachloride to 40 mole per cent carbon tetrachloride–60 mole per cent ethylene dichloride, it is obvious that the composition cannot be ascertained to such a high degree of accuracy for the reason that over this range the temperature change with change in composition is much less. Also, since the curve passes through a minimum at 70 mole per cent carbon tetrachloride–30 mole per cent ethylene dichloride, two different

compositions are possible for each boiling point. Over this range, therefore, it is essential to determine the specific gravity in addition to the boiling point. For mixtures having compositions between 80 mole per cent carbon tetrachloride–20 mole per cent ethylene dichloride and 60 mole per cent carbon tetrachloride–40 mole per cent ethylene dichloride, the composition can be determined more accurately by specific-gravity determinations, as over this range the change in boiling points with change in composition is very slight.

DISTILLATION OF BINARY MIXTURE CARBON TETRACHLORIDE-ETHYLENE DICHLORIDE

Since a boiling-point curve for mixtures of carbon tetrachloride and ethylene dichloride had been obtained, the determination of the composition of the vapor phase for all mixtures of these compounds was next attempted. The distillation apparatus used, a modification of which will be described in a subsequent publication, consisted essentially of the boiling-point apparatus mentioned above, to which was attached an equilibrium chamber suggested by the work of Rosanoff, Lamb, and Breithut (3). If one could add to the boiler of this apparatus a mixture having exactly the same composition as the initial portion of the distillate and continue the addition at the same rate as distillation proceeds, the composition and hence the boiling point of the solution would obviously remain constant, and the distillate would be identical in composition with the vapor of the original mixture at its boiling point. To approximate this condition the procedure described below was followed.

The distillation was carried out in two steps. During the first step the two constituents were added alternately in small increments while the boiling temperature of the solution was watched very closely. It was possible in this way to keep the boiling point constant to 0.05°C . After about 125 cc.

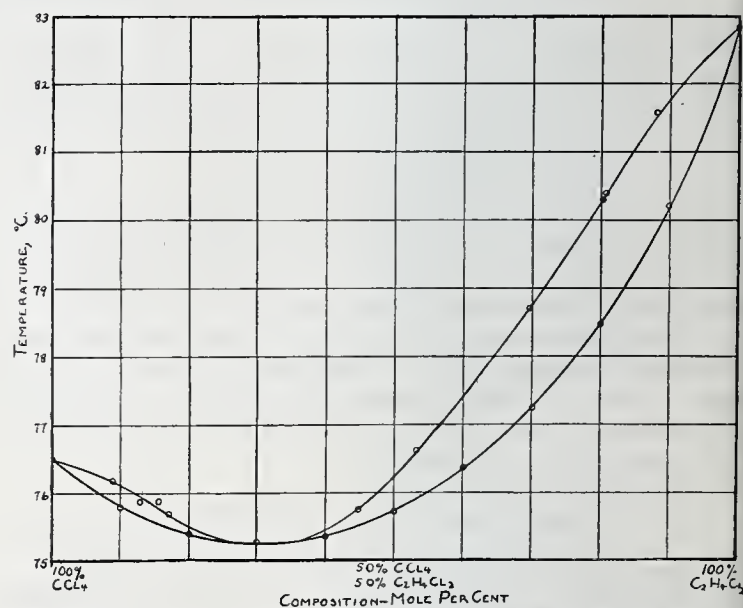


FIGURE 2. BOILING POINTS OF ETHYLENE DICHLORIDE AND CARBON TETRACHLORIDE AT DIFFERENT TEMPERATURES

had distilled over, the distillate was poured into a dropping funnel and returned to the boiler at the same rate as distillation proceeded. In this way it was easy, during the second stage of the distillation, to maintain the boiling temperature constant to within $\pm 0.01^\circ\text{C}$., indicating no change in concentration of the solution greater than 0.1 mole per cent.

The final distillate was analyzed by determining its boiling point and reading the ratio of the components from the curve of Figure 2. The composition of the boiling liquid with which this condensed vapor is in equilibrium was naturally determinable in the same way from its observed boiling point. The

results are tabulated in Table II and shown graphically in the upper curve of Figure 2. As is usual in systems having minimum boiling point, the vapor curve lies wholly above the liquid curve and bends to become tangent to it at the minimum boiling point. The composition of all corresponding liquids and vapors are given by the points on the curves having equal ordinates.

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RECEIVED June 24, 1931. Presented before the Division of Agricultural and Food Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

Optical Identification of Strychnine

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MOST of the chemical tests usually used for the detection of strychnine depend upon color reaction. As has been shown by Poe and O'Day (1), the color reaction with Mandelin's reagent is not specific and may be given by a number of organic compounds other than strychnine.

This paper describes a method for the detection of strychnine by means of the optical properties of some of its salts. A previous paper (2), in which the literature was reviewed, gives the optical-crystallographic data for a series of salts of strychnine. From the study of a number of these salts, it has been found that four, owing to their low solubility in water, are especially suitable for use in the optical detection of this alkaloid. These salts appear, together with some of their optical-crystallographic properties, in Table I.

TABLE I. OPTICAL PROPERTIES OF SEVERAL STRYCHNINE SALTS

COMPOUND	CLASS	REFRACTIVE INDEX, 25° C.			SYSTEM
		α	β	γ	
strychnine perchlorate	Biaxial	1.589	1.598 ^a	1.654	Monoclinic
strychnine hydrochloride	Biaxial	1.609 ^a	1.627	1.662	Orthorhombic
strychnine hydrobromide	Biaxial	1.646 ^a	1.650	1.730 ±	Monoclinic
strychnine hydroiodide	Biaxial	1.657 ^a	1.665	1.730 ±	Monoclinic

^a Index in lengthwise direction.

METHOD OF DETECTION

The sample of suspected material is purified in the usual manner by means of organic solvents. It is finally extracted with pure chloroform from an alkaline solution. The chloroform is then evaporated and the strychnine is dissolved in a small amount of 5 per cent acetic acid. The amount depends upon the quantity of strychnine present. The solution is divided into four equal parts, each of which should contain at least 0.25 cc. of solution with a strychnine content of about 0.5 mg. The amount of strychnine in solution may require adjusting by concentration or dilution. If the quantity is too small, no strychnine salt will separate out after the addition of the reagent and, if too concentrated, the crystals will be too small. After being divided, the solutions are placed in 50-cc. beakers and heated to boiling. They are tilted before the reagents are added so that the solutions will collect in a small area. To the first portion is added a slight excess of perchloric acid (or potassium perchlorate), the whole is warmed, and allowed to crystallize out very slowly. The liquid is removed and the crystals are washed with one drop of water. The filtrate and water may be carefully soaked up with filter paper, or a microfilter may be prepared by placing a small plug of absorbent cotton in the tip of a medicine dropper and drawing the liquid into the dropper. The crystals are allowed to dry in the air and are then mounted in oil of a refractive index of 1.598. If the crystals are strychnine perchlorate, they will show the same refractive index as the

oil—i. e., they will not be visible when the long direction of the crystal is parallel to the direction of vibration of the lower nicol prism (the 6 o'clock and 12 o'clock direction in the ordinary polarizing microscope.) The remaining two refractive indices may also be determined by substituting liquids of the proper refractive index. These determinations, however, require a petrographic microscope and some knowledge of optical mineralogy.

In a like manner the remaining portions may be tested by adding an excess of potassium chloride, potassium bromide, and potassium iodide, respectively. An excess of the salts may be added so as to reduce the solubility of the strychnine salt. Care must be taken, however, that the concentration is not so great as to cause the alkali halide to precipitate out when cold. If this should happen, these halides may be recognized immediately under the microscope, since all of them are isotropic. After the strychnine salt has been washed and dried, the crystals are submerged in oils of the proper refractive indices and the refractive indices of the crystals thus determined. The proper oil may be selected by referring to the indices given in Table I. It is often difficult to get all three of the refractive indices for a given crystal. In such cases finely divided glass wool may be used to obtain the crystals in an end position.

If desired, tests may be extended to other salts of strychnine. The four selected are the most satisfactory because of their slight solubility and because the refractive indices are readily determined, especially when the elongated crystal is oriented with its long axis parallel to the direction of vibration of the lower nicol. The alkaloid itself may be used, but it presents more difficulties than the above-mentioned salts.

After the presence of strychnine has been determined, it is well to repeat the determination and, at the same time, perform the tests with a suitable amount of strychnine of known purity.

In addition to the refractive indices, other optical tests, such as habit, sign, extinction, elongation, interference figures, polarization colors, optical angle, dispersion, etc., may be determined.

A number of alkaloids, which may be extracted in the same group with strychnine, such as atropine, codeine, brucine, morphine, etc., were studied. None of these showed enough interference to vitiate the test.

It appears that the above-described tests, together with the ordinary color tests, give a conclusive means for the positive identification of strychnine, even if the refractive index in the lengthwise direction only is determined.

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RECEIVED August 11, 1931.

Fuel-Gas Analysis for Heating Value and Combustion Calculations

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THE immediate objectives in calculating the efficiencies of combustion in gas-fired equipment are the ratio of flue gas to fuel gas, the ratio of air to fuel gas, and the amount of water formed in combustion. The ease of determining these factors is greatly increased if the complete chemical analysis of the fuel gas can be directly determined.

In dealing with the more complex fuel gases, it is difficult to determine the data required for such calculations by any of the commonly used schemes of gas analysis. In analysis with the so-called Bureau of Mines apparatus (2), it is customary to determine separately the hydrogen and carbon monoxide contents but to group the other combustible components as "illuminants" and as "methane" and "ethane." In a majority of fuel gases, paraffin hydrocarbons other than methane and ethane are present of which this scheme takes no account. Furthermore, no information is obtained regarding the composition of the mixture of unsaturated hydrocarbons which is termed the "illuminants." Such an analysis is of little value as a basis for combustion calculations.

Numerous schemes for the analysis of fuel gases by liquefaction and subsequent fractional distillation have been developed. That of Podbielniak (5) is sufficiently convenient and simple to find considerable application in industrial laboratories. In this scheme the components of the gas are identified by their boiling points, and their quantities determined by plotting a distillation curve of the liquefied mixture.

The method of Podbielniak yields excellent data when applied to natural or refinery gases. When volatile gases such as hydrogen or carbon monoxide are present, the fractional distillation must be supplemented by other methods in order to determine completely the composition of the combustible components. If considerable quantities of the pentanes or heavier hydrocarbons are present, differentiation between the higher boiling components is difficult and the data become uncertain as a basis for combustion calculations. The cost of the equipment and maintenance is also relatively high and the manipulation somewhat slower and more difficult than in the use of absorption or combustion methods of analysis. For these reasons, liquefaction methods are not particularly feasible where only a generally applicable method of determining combustion characteristics is required.

A complete scheme of analysis combining liquefaction, absorption, and combustion methods has been described by Wood (8). The data obtained by this method are complete but the procedure is long and difficult.

It has been pointed out by Parr (4) and recently emphasized by Baxter (1) that the results of the Bureau of Mines type of analysis have more significance if the average molecular composition of the paraffin hydrocarbons is reported rather than assuming that only methane and ethane are present. The paraffin content of the gas is reported in terms

A TRIPLE-COMBUSTION scheme of fuel-gas analysis to be carried out with the so-called Bureau of Mines apparatus is described. By this method the average compositions and volumes of both the saturated and unsaturated hydrocarbons of a gas sample are determined. The results of such an analysis may be used as a basis for combustion calculations.

Equations are developed whereby the heating values of mixtures of either saturated or unsaturated hydrocarbon gases may be calculated from their average compositions. The heating value of a complex fuel gas may be calculated from the results of a triple-combustion analysis with an error not ordinarily exceeding 2 per cent.

of a hypothetical compound C_nH_{2n+2} representing the average composition of the saturated hydrocarbons. The index number, n , may be evaluated from the data of the usual combustion analysis. This type of data is admirably suited for calculations of all kinds. From it, if the complete composition of the remainder of the gas is known, may be calculated the density and heating value as well as the stoichiometric relationships involved in combustion.

Unfortunately no simple and satisfactory methods have been devised for separating and identifying the unsaturated

hydrocarbons of a gas. In many fuel gases these unsaturated compounds contribute more than 30 per cent of the heating value of the gas. Since this fraction may include compounds of widely varying molecular weights and characteristics, it is evident that a means of determining the composition of the illuminants is necessary in any analytical scheme on which combustion calculations are to be based.

Calculation of the heating value of a fuel gas from its chemical analysis is ordinarily not possible because of the uncertainty regarding the composition of the illuminants. If the composition of the illuminants is determined by a liquefaction method, or if illuminants are absent, the heating value may be predicted with an accuracy sufficient for all ordinary requirements. Wojcicki (7) compared heating values calculated from chemical analysis to those experimentally determined for Polish natural gases in which no unsaturated compounds were present. The heating values were calculated on the basis of the index numbers of the paraffins present. It was found that these results differed by less than 1.0 per cent from those calorimetrically determined. Calculation of heating value from chemical analysis is particularly valuable when only samples of limited size are available for laboratory examination.

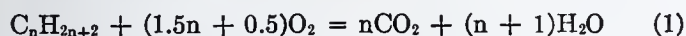
TRIPLE-COMBUSTION METHOD OF ANALYSIS

By extending the procedure ordinarily followed with the Bureau of Mines apparatus to include an additional total combustion with oxygen, data may be obtained from which the complete average compositions of both the paraffins and the illuminants may be calculated. No additional equipment is needed and the time required for the complete analysis is increased by only about 25 per cent.

The sample is first submitted to the complete procedure of the Bureau of Mines method (2). The carbon dioxide is absorbed in potassium hydroxide solution, the illuminants in fuming sulfuric acid, and the oxygen by phosphorus or alkaline pyrogallate. The carbon monoxide and hydrogen are determined by fractional combustion with cupric oxide at 300° C., followed by the determination of the carbon dioxide formed. The carbon monoxide content of the original gas is equal to the carbon dioxide formed, whereas the hydrogen

content is equal to the contraction in volume accompanying this first combustion.

The residual gas is assumed to consist of paraffin hydrocarbons and nitrogen. This gas is completely burned by introducing it into a pipet filled with pure oxygen in contact with a spiral of incandescent platinum wire. The contraction in volume and the carbon dioxide formed in the combustion are determined. From these data the volume and average composition of the paraffins may be calculated (4). The combustion reaction is as follows:



If V is the volume of the paraffins in the sample, the equations for the contraction and carbon dioxide formed in the combustion are represented, respectively, by

$$\Delta v = 1.5V + 0.5Vn \quad (2)$$

$$CO_2 = Vn \quad (3)$$

where Δv is the contraction in volume accompanying the second combustion. Combining Equations 2 and 3,

$$V = \frac{\Delta v - 0.5 CO_2}{1.5} \quad (4)$$

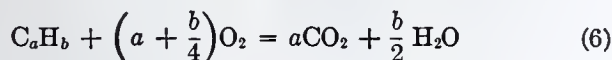
$$n = \frac{CO_2}{V} \quad (5)$$

The nitrogen content of the original sample is determined by difference, as usual.

For determining the composition of the illuminants, a second sample is taken into the apparatus, treated with potassium hydroxide solution to remove the carbon dioxide, and completely burned in the slow-combustion pipet with an excess of pure oxygen. The size of the sample to be taken for this third combustion depends on the oxygen demand of the gas. It is desirable to use as large a sample as possible without the volume of the products of combustion and excess oxygen exceeding the capacity of the buret. In working with the usual types of manufactured city gas, a sample of about 35 cc., burned with 90 cc. of pure oxygen, will be satisfactory.

The contraction in volume and the carbon dioxide formed in the combustion are determined and calculated to the basis of 100 cc. of the original gas. By means of these data the average composition of the illuminants may be calculated as follows:

In 100 cc. of the original gas there are V' cc. of unsaturated compounds having an average composition C_aH_b . When burned with oxygen, the following reaction takes place:



The contraction, $\Delta v'$, and the carbon dioxide resulting from the combustion of the illuminants contained in 100 cc. of the original gas are, respectively,

$$\Delta v' = V' \left(1 + \frac{b}{4}\right) \quad (7)$$

$$CO_2' = V'a \quad (8)$$

The contraction resulting from the combustion of the illuminants may be obtained as the difference between the contraction in volume accompanying the third combustion of the entire gas and the sum of the contractions resulting from the combustion of the carbon monoxide, hydrogen, and the paraffins. The contraction from the combustion of the paraffins is measured in the second combustion as Δv , based on a sample of 100 cc. From the combustion of the carbon monoxide and hydrogen there will be contractions equal to respectively one half and three halves of the volumes of these components in the sample. Thus,

$$\Delta v' = \Delta v'' - [\Delta v + 1/2CO + 3/2H_2] \quad (9)$$

where $\Delta v''$ = contraction in third combustion per 100 cc. of original gas sample

CO = percentage of CO in sample

H₂ = percentage of H₂ in sample

Since V' , the volume of the illuminants, is determined by absorption in fuming sulfuric acid, combination of Equations 7 and 9 permits direct solution for b .

The volume of carbon dioxide formed from the combustion of the illuminants is the difference between the carbon dioxide formed in the third combustion and the sum of the volumes of carbon dioxide formed from the paraffins and the carbon monoxide. That resulting from the paraffins is measured in the second combustion and is equal to Vn , from Equation 3. Thus,

$$CO_2' = CO_2'' - (Vn + CO) \quad (10)$$

where CO_2'' = CO₂ formed in third combustion per 100 cc. of sample

Combination of Equations 8 and 10 permits direct solution for a .

The application of this method is illustrated by the following data from the analysis of a typical carbureted water gas:

BUREAU OF MINES ANALYSIS		
	VOLUME Cc.	CONTRACTION
Original sample	100.0	
After KOH	97.4	2.6 = % CO ₂
After H ₂ SO ₄	90.3	
After KOH	89.0	8.4 = % illuminants
After P	88.3	0.7 = % O ₂
After CuO (1st combustion)	48.4	39.9 = % H ₂
After KOH	15.5	32.9 = % CO
O ₂ added for combustion	81.1	20.9 = Δv
After combustion (2nd combustion)	75.7	11.5 = CO ₂
After KOH	64.2	
TOTAL COMBUSTION (THIRD COMBUSTION)		
Volume of sample	33.0	
After KOH	32.2	
O ₂ added for combustion	91.8	
After combustion	85.9	38.1
After KOH	63.7	22.2

From Equations 4 and 5 and the data of the second combustion,

$$V = \frac{20.9 - 5.75}{1.5} = 10.1$$

$$n = \frac{11.5}{10.1} = 1.14$$

In the total combustion,

$$\text{Contraction per 100 cc. of gas} = \frac{38.1}{0.330} = 115.4 = \Delta v''$$

$$CO_2 \text{ formed per 100 cc. of gas} = \frac{22.0}{0.330} = 67.3 = CO_2'$$

From Equations 9 and 10,

$$\Delta v' = 115.4 - [20.9 + 16.4 + 59.8] = 18.3$$

$$CO_2' = 67.3 - [11.5 + 32.9] = 22.9$$

From Equations 7 and 8

$$b = \left(\frac{18.3}{8.4} - 1\right)4 = 4.72$$

$$a = \frac{22.9}{8.4} = 2.73$$

COMPLETE ANALYSIS

	%
CO ₂	2.6
C _{2.73} H _{4.72} (illuminants)	8.4
O ₂	0.7
H ₂	39.9
CO	32.9
C _{1.14} H _{4.28} (paraffins)	10.1
N ₂	5.4
	100.0

CALCULATION OF HEATING VALUE

The heating values of the lower paraffin hydrocarbon gases are represented by the following equations with errors of less than 0.5 per cent. These equations were derived from the data of the International Critical Tables and the recent experimental values of Rossini (6).

Total Heating Value:

$$\text{Gram calories per gram mole} = 156,700n + 56,100 \quad (11)$$

$$\text{B. t. u. per cu. ft. at } 60^\circ \text{ F., 30 in., satd. H}_2\text{O} = 732n + 262 \quad (12)$$

Net Heating Value:

$$\text{Gram calories per gram mole} = 146,200n + 45,500 \quad (13)$$

$$\text{B. t. u. per cu. ft. at } 60^\circ \text{ F., 30 in., satd. H}_2\text{O} = 683n + 212 \quad (14)$$

The heating values of the lower unsaturated hydrocarbon gases of average formula C_nH_b are satisfactorily represented by the following formulas, which were derived from the data of Kharasch (3):

Total Heating Value:

$$\text{Gram calories per gram mole} = 98,200a + 28,200b + 28,800 \quad (15)$$

$$\text{B. t. u. per cu. ft. at } 60^\circ \text{ F., 30 in., satd. H}_2\text{O} = 459a + 132b + 135 \quad (16)$$

Net Heating Value:

$$\text{Gram calories per gram mole} = 98,200a + 22,900b + 28,800 \quad (17)$$

$$\text{B. t. u. per cu. ft. at } 60^\circ \text{ F., 30 in., satd. H}_2\text{O} = 459a + 107b + 135 \quad (18)$$

The errors in the use of these equations are shown in Table I, in which values calculated from Equation 15 are compared to those taken from a critical compilation by Kharasch (3).

It will be noted that these equations break down entirely when applied to acetylene. However, for the lower olefins and aromatics, the equations represent the heating values within the probable accuracy of the experimental data.

The heating values of hydrogen and carbon monoxide from the data of Rossini (6) are as follows:

HYDROGEN

Total Heating Value:

$$\text{Gram calories per gram mole} = 68,310$$

$$\text{B. t. u. per cu. ft. at } 60^\circ \text{ F., 30 in., satd. H}_2\text{O} = 319$$

Net Heating Value:

$$\text{Gram calories per gram mole} = 57,750$$

$$\text{B. t. u. per cu. ft. at } 60^\circ \text{ F., 30 in., satd. H}_2\text{O} = 270$$

CARBON MONOXIDE

$$\text{Gram calories per gram mole} = 67,620$$

$$\text{B. t. u. per cu. ft. at } 60^\circ \text{ F., 30 in., satd. H}_2\text{O} = 316$$

By means of the above data and Equations 11 through 18, it is possible to calculate the heating value of a complex fuel gas from the results of the triple-combustion method of analysis previously described. This method is illustrated by the following calculation of the total heating value of the carbureted water gas whose analysis is given above:

Basis of calculation = 1.0 gram mole of fuel gas

$$\text{H. V. of hydrogen} = 0.399 \times 68,310 = 27,250$$

$$\text{H. V. of carbon monoxide} = 0.329 \times 67,620 = 22,250$$

$$\text{H. V. of unsaturated } C_{2.73}H_{4.72} = 0.084 (2.73 \times 98,200) + (4.72 \times 28,200) + 28,800 = 36,400$$

$$\text{H. V. of paraffins } (C_{1.14}H_{4.28}) = 0.101 (1.14 \times 156,700) + 56,100 = 23,750$$

$$\text{Total H. V., gram calories per gram mole} = 109,650$$

This calculated result corresponds to 512 B. t. u. per cubic foot measured at 60° F., 30 inches of mercury, and saturated with water vapor. The actual heating value of the gas indicated by a calibrated recording gas calorimeter was 518 B. t. u. per cubic foot. The error in the heating value calculated from the chemical analysis was -1.2 per cent.

TABLE I. TOTAL HEATING VALUES OF UNSATURATED HYDROCARBON GASES

GAS	(Unit: gram calories per gram mole)		ERROR %
	EXPERIMENTAL H. V.	H. V. CALCD. FROM EQ. 15	
Ethylene	338,000	338,000	0.00
Propylene	490,200	492,600	+0.49
Isobutylene	647,200	647,200	0.00
Amylene	808,700	801,800	-0.85
Benzene	787,200	787,200	0.00
Toluene	944,000	941,200	-0.3
Acetylene	312,000	281,600	-9.7

ACCURACY OF METHOD

It must be recognized that the methods described above are subject to the limitations of the grade of commercial gas-analysis equipment usually employed. The average composition of the unsaturated hydrocarbons is determined from differences between relatively large experimentally determined values. This result is particularly uncertain when the unsaturated hydrocarbons constitute only a small fraction of the total combustible components. However, in such cases accurate knowledge of the composition of these compounds is of correspondingly lesser importance. If reasonable care is used, the results of the analysis should be satisfactory as a basis for all ordinary combustion calculations.

In carrying out the analysis particular care must be exercised that the two samples used are of exactly the same composition. The samples should be stored over mercury, out of contact with rubber tubing or stoppers which might absorb hydrocarbons. Mercury must be used in the buret and combustion pipet of the analytical apparatus. When the heavier hydrocarbons are present, care must be taken that each combustion with oxygen is complete. The mixture of excess oxygen and combustion products should be repeatedly passed into the combustion pipet over the incandescent platinum spiral and returned to the buret for measurement until a constant volume is attained. By heating the spiral only when gas is being passed into the pipet, this can be accomplished with minimum opportunity for oxidation of nitrogen.

The accuracy of the heating value calculated from the analysis is dependent largely on the accuracy of the analysis and on the accuracy of the determinations of the heating values of the pure components on which Equations 11 through 18 are based. There is considerable uncertainty as to the heating value of pure ethylene. The value given in Table I is an average of two values given by Kharasch which differ from each other by over 4 per cent.

If reasonable care is used in the analysis, it is believed that the calculated heating value will rarely deviate from the correct one by more than 2 per cent unless a large amount of acetylene is present. In several tests of the method on carbureted water gases, this limit of error was not exceeded. In working with heavy gases which burn with difficulty in the combustion pipet, somewhat larger errors may be encountered.

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Stability Test of Nitroglycerin-Nitrocellulose Smokeless Powder

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IN A RECENT article Lenze and Metz (9) have discussed the value of various stability tests used for single-base powders.¹ A few powders of widely varying stability were chosen and compared. It could be concluded from their data that a good powder and a bad powder were distinguishable readily by almost any of the ordinary tests. The relative value of various tests has also been very ably discussed by de Bruin (5). Up to the present, no single test has been found to be entirely satisfactory for judging the probable life of a powder.

In the case of double-base powders, the problem is complicated further by the volatility of nitroglycerin during the test. If a low temperature is used in order to obviate this difficulty, the time required for testing the powder is too great to be of practical significance. The "trace tests," such as the Abel (1) and Guttmann (8) tests, in which a sensitive paper is used to detect the first evolution of nitric oxide, are carried out at a fairly low temperature, but are of doubtful value for gelatinized powders. The quantitative determination of the products of decomposition at ordinary temperatures, as in tests proposed by Chiaraviglio and Corbino (6) and Pollard (10), have the advantage that the powder is tested under normal temperature conditions, but it cannot be recommended for general use because of the elaborate apparatus required and the high technic necessary to obtain accurate results.

Of the quantitative tests the methyl violet, surveillance, Bergmann-Junk-Mayrhofer (4), and Taliani (11) may be mentioned as being representative of those most free from objection. No special technic must be acquired to carry on the tests, a very desirable characteristic for control purposes. The products of decomposition remain in contact with the powder during the course of the tests. These tests, together with the Abel test at 82.2° C., have been used in this investigation for examination of the condition of a number of

DESCRIPTIONS are given of five stability tests for double-base powders. Modifications were made in the method and apparatus for carrying out the Taliani test, which made the test somewhat simpler to operate.

Specifications are given for a division between stable and unstable powders by the surveillance, Taliani, and B. J. M. tests. If a single test is run preference is given to the Taliani test. However, it is suggested that a surveillance test be made on questionable powders.

All the tests were somewhat dependent on the nitroglycerin content of powders, the Taliani test, however, being least affected.

double-base powders of varying nitroglycerin content and various age.

In all of these tests there is some volatilization of nitroglycerin, as is shown by the dependence of the results on the nitroglycerin content of the powders. Nevertheless, certain of the tests afford a useful method for distinguishing between good and bad powders with a fair degree of reliability.

DESCRIPTION OF TESTS

SURVEILLANCE TEST. The surveillance test was carried on at 78° C. Forty-five grams of the powder were weighed into a dry flint-glass 8-ounce (0.23-liter) bottle which had been carefully cleaned by washing with acetone and ether, followed by long steeping in boiling distilled water. The glass stoppers were ground to fit with emery slime. The bottles were placed in a deep double-walled oven provided with a close-fitting lid. Alcohol was used as the heating liquid and was maintained at the boiling point by means of a steam coil in the liquid. A condenser at the top of the jacket prevented loss of the alcohol. The samples were examined daily and were removed when brown fumes were observed above the powder.

It was found advisable to use a temperature of 78° C. instead of the usual 65° C., in order to obtain dependable results. The variation in test between duplicate samples at 65° C. was so great that a clear differentiation between samples was not always possible. Further, the time required to carry on a test at 65° C. is too long for a practical test.

TALIANI TEST. The procedure and apparatus were modifications of those proposed by Taliani. A double-walled copper bath, provided with a double door, was built (Figures 1 and 2). A glass window was built into each door, and directly in line with these a double glass window was built into the back wall of the bath. This permitted an unimpaired view of the capillary tubing inside the bath. A well, 1.25 inches (3.17 cm.) in diameter and 2 inches (5.08 cm.) deep, was welded into the bottom of the bath. Between the outer

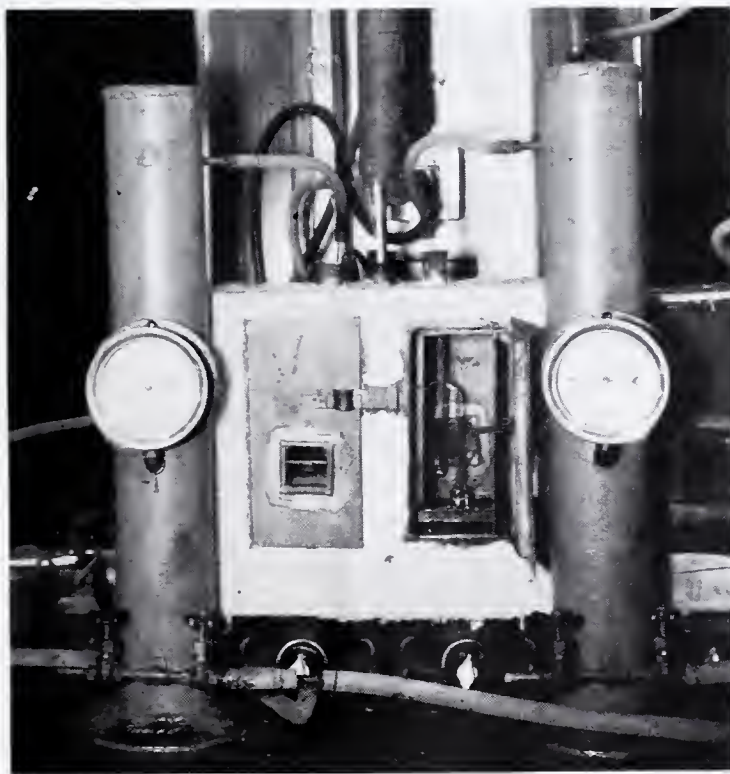


FIGURE 1. TALIANI TEST BATH

¹ In conformity with general terminology in this country, single-base powders refer to powders in which the main constituent is nitrocellulose. Double-base powders include those made of nitrocellulose and nitroglycerin as the main constituents.

and inner walls of the bath, a mixture of glycerin and water, boiling at $120^{\circ} \pm 0.3^{\circ} \text{C.}$, was used.

The sample is placed in a special test tube (Figure 3) to which is attached a U-bend containing Nujol (a high-boiling neutral paraffin oil). The capillary is attached to a pressure cylinder, which is connected through a needle valve to the service air line. The pressure cylinder is provided with a

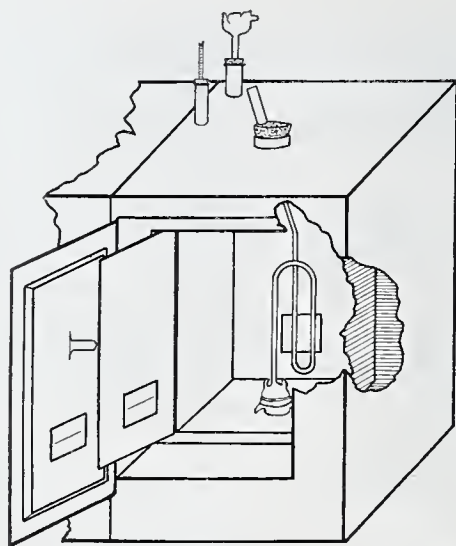


FIGURE 2. DIAGRAM OF TALIANI TEST BATH

gage by means of which the pressure in the apparatus is followed. In the early part of the work the seal between the test tube and the cap was made by a ground-glass joint. This arrangement, used by Taliani, was unsatisfactory because of leaks through the joint. This was obviated by use of a mercury seal inside the tube. When covered by a small amount of Nujol, the mercury remained unattacked during the test. The tube was tied to the cap by tightly drawn wires secured to projections. In the original Taliani capillary, a stopcock was attached to the tube above the cap to carry off moisture and air evolved in the first part of the test. This stopcock was found to be a continuous source of uncertainty during the latter part of the test when the pressure increased to several pounds. The stopcock has been eliminated and any moisture or air is allowed to escape through the capillary, and, at the end of the preliminary heating, the Nujol is introduced through the open end of the capillary. The volume of the tube and capillary to the point B is exactly 12 cc.

As it is difficult to see a mark etched on the capillary at the point B, horizontal lines are etched on the glass in the door of the bath and in the glass window in the rear wall. By controlling the pressure in the cylinder, the level of Nujol can be brought in line with the two marks.

All powders are well dried over calcium chloride and sodium hydroxide before testing. One gram of powder is weighed into the test tube. The tube and capillary, tied together as described above, are introduced into the bath, the outlet of the capillary passing through an opening in the top of the bath, the test tube resting in the well of the bath. The space between the test tube and the well is filled with Nujol to improve heat transfer. After exactly 30 minutes' heating, a few drops of Nujol are introduced into the top of the capillary and the connection made to the pressure cylinder by rubber tubing. Air is turned into the pressure cylinder until the Nujol thread is forced to the point B (Figure 3). The reading of the gage is taken as the zero reading and is subtracted from all succeeding readings. As the pressure builds up in the powder tube, it is equalized by admitting air to the pressure cylinder. Readings of time and pressure are taken at each 0.5 pound pressure increment. Plots of some representative data are

given in Figure 4. The test is reported as the time required for the pressure to increase 8 pounds above starting pressure. When the test is completed, the pressure is released from the tank through a needle valve and the rubber tubing disconnected.

BERGMANN-JUNK-MAYRHOFER TEST. The usual Bergmann-Junk stability tubes as described by Worden (14) are used. Instead of the special bath described by Worden, an A. S. T. M. bath (2) is used. The decomposition tube is immersed in the bath within 2 inches (5.08 cm.) of the top. The adsorption cup is surrounded by a shield to avoid undue cooling of the short connection between the cup and the decomposition tube. Bergmann and Junk have recently called attention to this source of error (3). The bath temperature was maintained at $120^{\circ} \pm 0.3^{\circ} \text{C.}$ by means of a mixture of glycerin and water.

Two grams of powder, well dried over concentrated sulfuric acid, are weighed into the decomposition tube. Ten cubic centimeters of 5 per cent potassium iodide solution are placed in the absorption cup, and after lightly greasing the ground-glass connection, the cup is attached to the tube. The whole is placed in the test bath, the wells of which contain Nujol. The protecting shield is put in place and the tubes are heated for exactly 6 hours. At the end of the test, the tubes are removed, 10 cc. of distilled water are added, and on cooling the liquid is drawn into the decomposition tube. After 10 to 15 minutes' cooling, a clean rubber stopper is fitted into the top of the absorption cup and the whole shaken vigorously for several minutes. This absorption cup is rinsed with distilled water and the rinsings are added to the liquid in the decom-

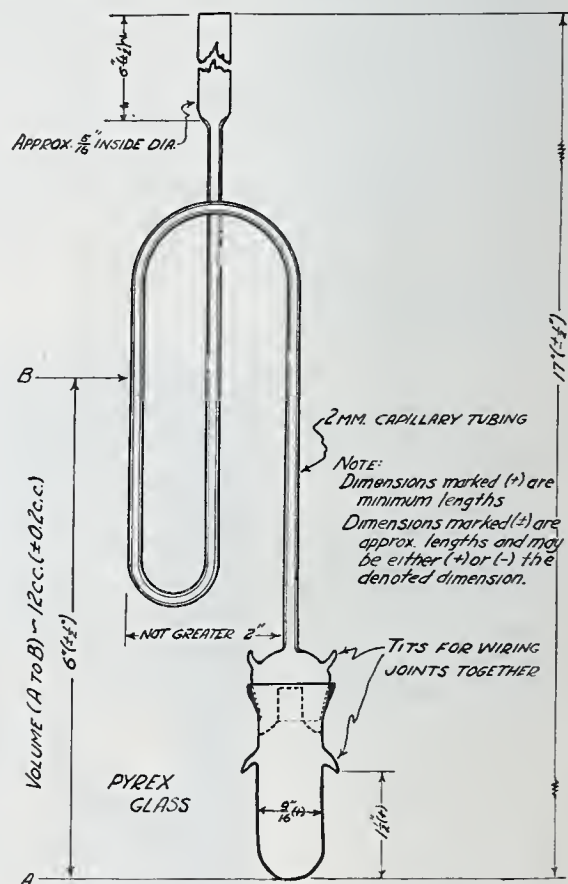


FIGURE 3. TALIANI TEST TUBE

position tube. The volume is made up to 50 cc., and after vigorous mixing an aliquot of 25 cc. is withdrawn and titrated with 0.01 N sodium thiosulfate. The nitric oxide equivalent to the thiosulfate is calculated and reported as milligrams of nitric oxide per gram of powder for 6 hours' heating.

de Bruin (5) points out that in the B. J. M. test there is a possibility of adsorption of iodine by the powder. With

poorly gelatinized powders this was found to be the case, but with well-gelatinized powders the amount of iodine adsorbed from a solution of concentration equal to that in a usual test was found to be equivalent to less than 0.1 mg. of nitric oxide per gram of powder. This is within the limit of error of the B. J. M. test and has a negligible effect on the results of the test. The amount of nitroglycerin had no appreciable effect on the adsorption when well-gelatinized powders were used.

METHYL VIOLET TEST AT $134.5^{\circ} \pm 0.5^{\circ} \text{C.}$ (15). Two and five-tenths grams of powder are weighed into a test tube 29 cm. long and 15 mm. inside diameter with walls 1.5 mm. thick. A test paper prepared as described by Worden (13) is inserted in the tube about 1.5 inches (4.3 cm.) above the sample. The tube is placed in the well of an A. S. T. M. bath, there being enough Nujol in the well to fill completely the space between the tube and the well. After 10 minutes the tube is inspected each minute until near the end point, when the tube is inspected at 30-second intervals. The use of Nujol in the wells permits much more frequent inspection of the samples without appreciably affecting the test than when air fills the space between the tube and the well. The time from the insertion of the sample into the bath until the test paper is turned salmon pink throughout is taken as the methyl violet test.

POTASSIUM IODIDE AT 82.2°C. This is merely the Abel test (12) carried out at a higher temperature. The 65°C. test proved unsatisfactory from the standpoint of duplication of results. When the temperature was raised to 82.2°C. better duplication was obtained.

DISCUSSION OF RESULTS

The data on a series of powders are given in Table I. Samples 1, 2, 5, and 6, made without stablizer, appear quite unstable by the surveillance, Taliani, and B. J. M. tests. From the methyl violet test they would be considered stable. Samples 2 and 5 appear stable by the potassium iodide test, whereas 1 and 6 seem unstable. Sample 13 was 22 years old when tested and proved unstable by the surveillance, Taliani, and B. J. M. tests, but appeared of satisfactory stability by the methyl violet and potassium iodide tests. Sample 14 was made prior to 1913, and gave a similar result. Samples 17 and 19 would be considered stable by the methyl violet, potassium iodide, and B. J. M. tests, but definitely unstable by the surveillance and Taliani tests. The available diphenylamine determination supports the view that these two powders are

unstable. In the case of the methyl violet test, volatilization of nitroglycerin and decomposition of the latter in the vapor state and on the surface of the test paper undoubtedly play a preponderant role. The potassium iodide test, on the other hand, is not affected to the same extent by this particular

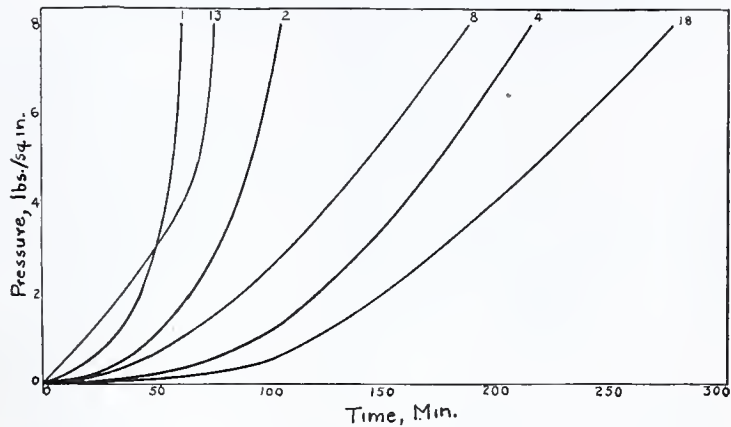


FIGURE 4. TALIANI TEST CURVES. 1, 2, 13, unstable powders; 4, 8, 18, stable powders

variable, but fails to give results in conformity with the known condition of the powder. It will be generally admitted that powders made with stabilizer have a longer life under normal storage conditions than powders made without stabilizer. A test which fails to differentiate clearly between such powders is unsafe to use. For this reason the methyl violet and potassium iodide tests cannot be recommended for use in arriving at the probable storage life of double-base powders.

The relative value of the surveillance, Taliani, and B. J. M. tests can, perhaps, be brought out best by correlation charts of the results of the tests, Figures 5, 6, and 7. When the results of surveillance and Taliani tests (Figure 5) are plotted, the chart may be divided into four sections, A, B, C, and D. Powders in section C are undoubtedly stable, and those in section A unstable. Any powders represented in sections B or D are of doubtful stability and should be tested frequently. There is a wider spread between the values for stable and unstable powders by the Taliani test than by the surveillance test. This chart serves to establish limits between stable and unstable powders. Any powder giving a surveillance test of 25 days or more may be regarded as stable by this test. A stable powder will give a Taliani test above 150 minutes. It

TABLE I. STABILITY DATA

SAMPLE	YEAR MADE	YEAR TESTED	PER CENT NG	STABILIZER		SURVEILLANCE ^a	TALIANI ^b	B. J. M.	METHYL VIOLET	POTASSIUM IODIDE ^c	REMARKS
				%	Days						
1	1929	1930	40	0	4-4	60-65	10.2	14	10		
2	1929	1930	40	0	4-4	104-106	9.5	15	30		
3	1929	1930	40	0.5 No. 1d	36-39	239-228	5.2	16	11		
4	1929	1930	40	0.5 No. 2d	32-34	218-218	5.2	16	12		
5	1929	1930	40	0	5-5	80-81	7.6	15	22		
6	1929	1930	40	0	6-9	89-88	8.2	15	8		
7	1926	1930	40	0.75e	33-39	177-182	4.1	15	11		
8	1926	1930	40	0.75e	34-35	189-192	4.8	15	14		
9	1926	1930	40	0.75e	32-35	199-194	4.4	13	12		
10	1926	1930	40	0.75e	43-52	158-159	4.6	15	11		
11	1929	1930	40	0.50e	23-23	258-241	5.9	15	45		
12	1929	1930	40	0.50 No. 1d	28-30	242-247-240	6.0	16	8		
13	1908	1930	40	?	17-17	77-75	8.9	21	25		Probably made without stabilizer
14	?	1930	40	?	22-22	67-76	10.5	18	20		Made before 1913
15	1914	1930	40	0.30e	34-36	276-291	4.5	18	14		
16	1916	1930	40	0.30e	32-32	234-238	5.4	18	13		
17	1917	1930	40	0.50e	20-21	76-72	5.0	20	30		Available diphenylamine, 0.04%
18	1917	1930	40	0.50e	42-46	275-286	4.7	18	22		Available diphenylamine, 0.25%
19	1920	1930	40	0.47e	20-20	67-70	5.5	20	30		Available diphenylamine, 0.04%
20	1923	1930	40	0.47e	24-30-31	292-293	4.4	18	23		
21	?	1930	30	?	30-31	98-93	2.8	27	30		Made before 1913
22	1914	1930	30	0.30e	39-41	280-293	3.0	19	26		
23	1923	1930	30	0.50e	90-103	327-333	2.5	18	..		
24	1908	1930	30	?	23-23	136-137	2.0	29	12		Probably made without diphenylamine
25	1917	1930	20	0.30e	109-120	451-450	1.9	25	30		
26	1926	1930	20	0.75e	143-150	207-209	1.6	21	60+		
27	1929	1930	10	0.58e	108-132-148	400+	0.2	29	60+		
28	1929	1930	10	0.58e	135-151	400+	0.6	22	60+		

^a At 78° C.

^b At 120° C.

^c At 82.2° C.

^d Centralite.

^e Diphenylamine.

should be noted that these limits are for 40 per cent nitroglycerin powders. Section A, Figure 5, contains the four powders made without stabilizer, as well as the two oldest powders. Powders 17 and 19 appear unstable. The reason for this is not known, but the results are supported by the low available diphenylamine content of the samples.

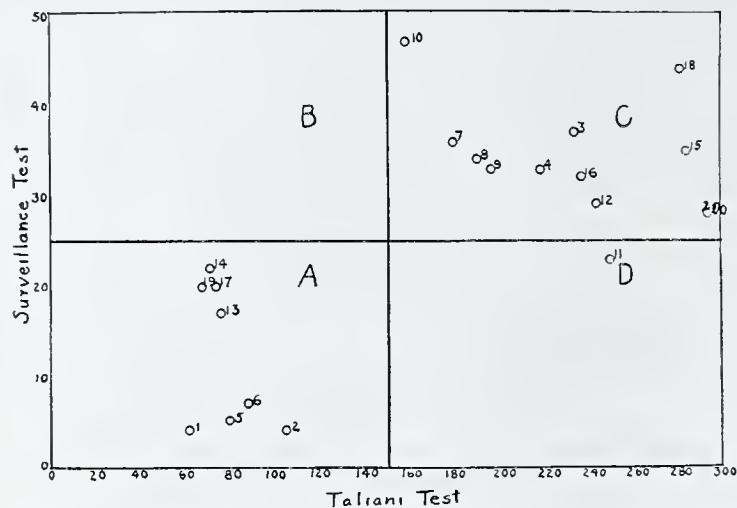


FIGURE 5. CORRELATION OF SURVEILLANCE AND TALIANI TESTS

Figure 6 gives the correlation between surveillance and B. J. M. results. The line of division between stable and unstable powders by the B. J. M. test is placed at a value of 6.5 mg. of nitric oxide. The powders without stabilizer, as well as the old powders, appear in the unstable group, while samples 17 and 19 have shifted to the doubtful group. Sample 11 also appears in this group. The remainder of the powders are considered stable. It will be noted that the same powders appear in the stable section as were found in the corresponding section of the preceding chart.

In Figure 7, the correlation between the B. J. M. and Taliani tests is given. The same grouping of powders is observed in this chart as was noted in Figure 6 with the exception of sample 11, which now appears in the stable group.

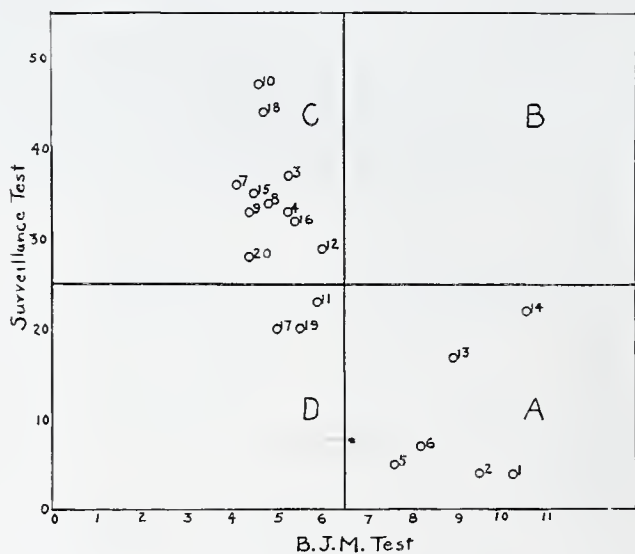


FIGURE 6. CORRELATION OF SURVEILLANCE AND B. J. M. TESTS

A critical comparison of the results of the B. J. M. with the surveillance and Taliani shows the former to be more a function of the nitroglycerin content than either of the latter. When diphenylamine was left out of the powder formula the fact is clearly brought out by the B. J. M. test, but not so strikingly as with the surveillance and Taliani tests. The two samples showing a very low available diphenylamine content were definitely unstable by the surveillance and Taliani tests but were satisfactory by the B. J. M. test.

From these comparisons, it is concluded that of the three tests, the B. J. M. is fairly satisfactory for judging the condition of a powder, but not so useful as the surveillance and Taliani tests. The surveillance test requires 25 days before a decision can be given as to the stability of a sample, while the Taliani test can be carried out within a few hours. For this reason the Taliani test is to be preferred. The data indicate, however, that the test is somewhat dependent on the nitroglycerin content and increases with a decreasing amount of nitroglycerin in the powder. This is an undesirable feature. As it seems to be less dependent on the nitroglycerin content than the other tests, it is probably as good as can be done at present. However, since the test is not entirely satisfactory, entire dependence cannot be placed in the result of a single method, and a check should be made as to the stability of the powder by another method. If time is available, the surveillance test is to be preferred, but the B. J. M. test may be used.

Some data are given for 30 per cent nitroglycerin powders. It is evident that the specifications for stable powders should be revised from those for the 40 per cent nitroglycerin type.

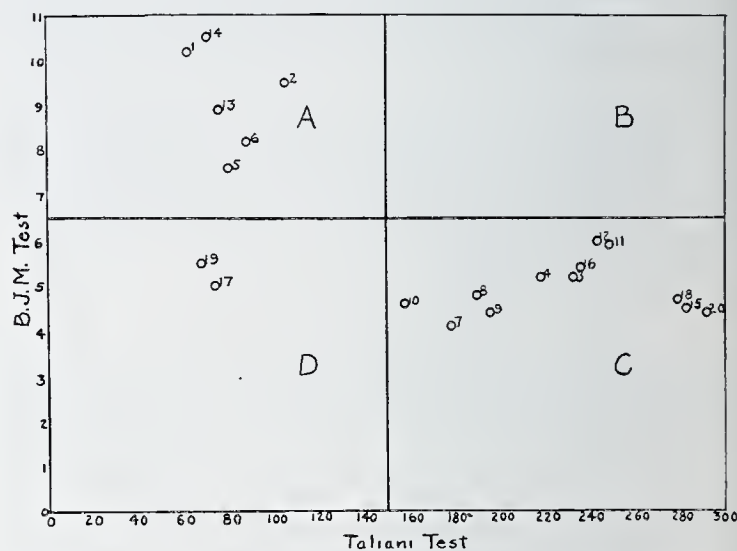


FIGURE 7. CORRELATION OF B. J. M. AND TALIANI TESTS

The B. J. M. test does not differentiate the powders so clearly as the Taliani and surveillance tests. There are insufficient data to fix specifications for the 30, 20, and 10 per cent nitroglycerin powders. However, until a long series of tests for each type is run, it is suggested that the same stability limits be adopted for these as is used for the 40 per cent nitroglycerin type. An unstable powder is readily noted, as in the case of sample 24.

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Explosion-Time Test of Double-Base Powders

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OF THE specifications placed on smokeless powder there are none more stringent and important than those covering the chemical stability. Many of the stability tests are based on measurement of traces of acidic products of decomposition. These products may react as a sensitive substance impregnated in an absorbent paper, as in the case of the Abel test, the methyl violet test, and the litmus test. If the test is carried on at temperatures above 100° C. the sample is commonly allowed to remain in the test bath until brown fumes of nitrogen tetroxide develop. The time for this result to be attained is noted, or the products may be absorbed in various liquids and determined subsequently by suitable means. The test may be carried out in a closed container at an elevated temperature and the time determined for visible fumes to develop above the powder sample (surveillance test). Other methods based on the rate of pressure development in a closed system have been proposed. Finally, a test in general use in this country depends on the determination of the time for a powder sample to explode when heated at 134.5° C. It is probable that no single test is entirely satisfactory for judging the condition of a given powder for chemical stability. The comparative value of the various tests for double-base powders¹ will be considered in another place; it is the purpose of this paper to point out the entire inadequacy of the explosion-time test for judging the chemical stability of nitroglycerin powders.

From a study of methods of measuring stability of smokeless powder, principally with those of the single-base type, Sy (2) gave the following limits for the explosion time at 135° C.:

Uncolloided nitrocellulose, no explosion in 5 hours
Nitrocellulose powders, no explosion in 5 hours
Nitroglycerin powders, no explosion in 5 hours

In the case of uncolloided nitrocellulose and nitrocellulose powders, these limits should be met, as it is well known that insufficiently stabilized nitrocellulose—i. e., nitrocellulose retaining traces of combined sulfuric acid—is very sensitive to heating at this temperature. Powders made from such nitrocellulose will, of course, be unstable. However, it will be shown that double-base powders made from well-stabilized nitrocellulose may give explosions in considerably less time than 5 hours and still be perfectly stable, in the usual sense, when certain chemically inert substances are added to the powder formula.

It is unfortunate that tests based on the work of Sy are still used in this country for double-base powders.

In conducting the test, 2.5 grams of powder are weighed into a glass test tube 15 mm. inside diameter and 29 cm. long, with tube walls 1.5 mm. thick. The tube is placed in an A. S. T. M. (1) heat-test bath and the time noted for the

BY CAREFUL control of the method of heating it is possible to obtain fairly accurate check results in the explosion-time test.

The absence of stabilizer from a powder formula is not detected by the explosion-time test, and this is not a function of the amount of nitroglycerin in the powder. Many salts lower the test markedly without lowering the storage life. Other salts have no effect. The effect seems to be limited to salts of the uni-univalent type, such as potassium nitrate. Metallic oxides increase the explosion test without improving the storage stability of the powders. Powders which were rendered unstable by long heating in a closed container gave satisfactory explosion tests.

As the explosion test does not measure the true stability of double-base powders, it is of no value in deciding their chemical condition.

sample to explode. If explosion has not occurred at the end of 5 hours, the tube is removed and the test reported as 300+ minutes.

Data obtained on a series of samples are given in Table I, and, for comparative purposes, data are given on surveillance and methyl violet tests. By these two tests all of the powders would be considered satisfactory, yet a number of them exploded in less than 5 hours. When only one test is given in the last column of the tables, the value is the average of two closely agreeing results. It will be shown in a subsequent paper that the surveillance test is of much greater value for judging the stability of double-base powders than the methyl

violet test, which detects only seriously decomposed powders.

It will be noted that in some cases there is an utter lack of agreement in the explosion time. This is due chiefly to differences in heat conductivity from the powder to the bath liquid. In one case the heat of decomposition is dissipated to the bath more quickly than in the other. The poor heat conductivity allows the sample to heat to its ignition temperature more rapidly. When a neutral paraffin-base oil was used in the wells surrounding the tubes (Bath A, Table III), better agreement in the results was obtained.² A special oil bath was built, heated by an immersed resistance coil and controlled by a thermostat to $\pm 0.05^\circ$ C. This closely controlled bath (Bath B, Table III) gave no more concordant results than the A. S. T. M. bath when oil was used in the wells of the latter.

TABLE I. COMPARATIVE STABILITY DATA

No.	NITRO-GLYCERIN %	KNO ₃ %	Ba(NO ₃) ₂ %	SURVEIL- LANCE AT 78° C.	METHYL VIOLET AT 134.5° C.	EXPLOSION TIME AT 134.5° C.
				Days	Min.	Min.
2	25	0.81	1.01	52	17	170
4	25	0.38	0.88	82	17	300+
6	25	0.45	1.06	68	17	160; 300+
10	25	0.57	1.31	58	17	300+
20	25	0.59	1.15	50	17	300+
32	35	0.50	1.50	56	16	300+
40	30	0.50	1.50	53	17	162; 300+
50	30	0.40	0.97	91	17	300+
78	30	0.50	1.50	55	14	150
79	30	0.50	1.50	71	13	163; 300+
80	30	0.50	1.50	52	14	150
81	30	0.50	1.50	44	14	150

A study of the effect of varying powder composition is given in Table II. In this case paraffin oil was used in the wells. When even small amounts of potassium nitrate are added to the formula, the explosion time is decreased markedly, although the methyl violet and surveillance tests indicate satisfactory stability. When diphenylamine was omitted from the formula, the surveillance test dropped to a low value,

² The oil used inside the wells should not be confused with the heating mixture of xylol and toluene used in the body of the bath. The latter is kept at its boiling point in order to maintain the bath at constant temperature. The paraffin oil merely replaces the air between the outside of the glass test tubes and the inside of the brass wells.

¹ Double-base powders refer to those containing nitrocellulose and nitroglycerin as the chief ingredients.

yet in the absence of potassium nitrate the powder would be considered stable by the explosion-time test.

TABLE II. EFFECT OF VARYING POWDER COMPOSITION

No.	NITRO-GLYCERIN	KNO ₃	Ba(NO ₃) ₂	DI-PHENYL-AMINE	METHYL VIOLET AT 134.5° C.	EXPLOSION TIME AT 134.5° C.	SURVEILLANCE AT 78° C.
	%	%	%	%	Min.	Min.	Days
952.1	40	0	0	0.1	16	300+	34
1060.1	40	2	0	0.5	15	140	23
673.3	40	0.5	1.5	0.75	15	150	36
673.7	40	0.5	1.5	0.75	15	146	34
673.10	40	0.5	1.5	0.75	13	157	33
679.17	40	0.5	1.5	0.75	15	119	47
951.1	40	0	0	0	15	300+	5
953.1	40	4	0	0	15	150	7

TABLE III. EFFECT OF TYPE OF BATH ON 40 PER CENT NITROGLYCERIN POWDERS

Lot No.	(Explosion test)	
	BATH A	BATH B
	Min.	Min.
146	347+	385+
165	267, 276, 258	268, 247, 289
166	347+	380, 385+
167	322, 347	313, 285
168	355+	362, 347, 378
170	317, 345+	291, 298

TABLE IV. EFFECT OF VARIOUS ADDITION AGENTS ON EXPLOSION TEST

(40% nitroglycerin powders; N. C. = 59.25% (N₂ = 13.08); diphenylamine = 0.75%)

No.	ADDED SUBSTANCE		METHYL VIOLET	EXPLOSION TIME AT 134.5° C.
		%	Min.	Min.
D-32			19.5	247; 265
D-40	KClO ₃	1	22	191
D-42	KClO ₃	2	20	125
D-43	KClO ₃	3	21.5	124
D-44	KClO ₃	4	21.5	123
D-48	KMnO ₄	4	9.5	29
1137	KMnO ₄	2	9	184; 192
1138	Ba(MnO ₄) ₂	2	12	300+
1117	Ba(NO ₃) ₂	2	17	300+
D-53	KNO ₃	4	20.5	80; 85
1116	NaNO ₃	2	17	190; 212
D-59	KCl	4	14	135; 134
D-57	NaCl	4	20.5	97; 94
1113	SrCl ₂	2	14	300+
D-55	K ₂ SO ₄	4	22	174; 177
D-58	MgSO ₄	4	13	260; 245
D-49	K ₂ Cr ₂ O ₇	4	20.5	250
D-36	MnO ₂	4	18	300+
1136	MgO	2	18.5	300+
D-50	PbO ₂	4	16.5	296
D-51	SnO ₂	4	19.5	300+
D-52	Fe ₂ O ₃	4	22.5	300+

From the preceding it is evident that the amount of nitroglycerin contained in the powder is not the controlling factor in this test. A number of salts and oxides were incorporated in a series of 40 per cent nitroglycerin powders. The data on these powders are given in Table IV. It is well known that traces of acid will cause failure of the powder in any of the stability tests. It was first thought that minute traces of decomposition products of the salts were responsible for the low explosion tests obtained. However, this view is untenable when it is recalled that many of the compounds were salts of strong acids and strong bases. Such compounds are extremely stable to hydrolysis and so would not develop either acid or base on heating to 135° C. The action of each salt on the test seems to be specific. The explosion test of D-32, made without added substance, is the result to which the other tests are referred. Potassium chlorate has a marked effect in lowering the test, and in amounts greater than 2 per cent the effect is not additive. If the effect of this compound were due to acidic decomposition, one would expect the test to fall off markedly with increase in amount. Two, three, and four per cent did not produce this result. When potassium permanganate is added, a powder of very low explosion test results. On the other hand, barium permanganate seems to be without effect. A similar relation

exists between potassium and barium nitrates. The chlorides give sensitive powders in the case of sodium and potassium, but not in the case of strontium. Sulfates have a smaller effect than either the nitrates or chlorides. The oxides lead to powders which are quite insensitive, probably because of absorption of the acid products of decomposition. The inclusion of such large amounts of basic oxides is not to be recommended, as powders so produced usually prove unstable by the surveillance test.

TABLE V. EFFECT OF VARYING PROPORTIONS OF POTASSIUM NITRATE AND FERRIC OXIDE

(40% nitroglycerin powder)

No.	KNO ₃	Fe ₂ O ₃	DIPHENYL-AMINE	METHYL VIOLET AT 134.5° C.	EXPLOSION TIME AT 134.5° C.
	%	%	%	Min.	Min.
915.1	4	0	0	15.5	150 157
916.1	2	2	0	15.5	151; 155
959	0.5	3.5	0	15.5	202; 230
960	0.25	3.75	0	15.5	235; 240
965	0.10	3.90	0	14.5	294; 315
966	0	4.0	0	14.5	410; 420+
967	0	0	0	14.5	318; 333
920.1	3.5	0.50	0.50	16.5	130; 133
918	3.0	1.0	0.50	16.5	150; 160
917	2.0	2.0	0.50	17	157; 165
919.1	1.0	3.0	0.50	16.5	163; 165

As potassium nitrate is a common oxidizing agent added to smokeless powders and, as it has a very definite effect in lowering the explosion test, it was of interest to determine the effect of relatively small amounts of this ingredient (Table V). The total added substance amounted to 4 per cent, being made up of a mixture of potassium nitrate and iron oxide. Potassium nitrate in an amount as small as 0.10 per cent has a distinct effect. The addition of diphenylamine as stabilizer does not give a powder of longer explosion test, although it improves the surveillance test several hundred per cent. Potassium nitrate has been added to powders for many years, and records of this laboratory do not show a single case of such powders failing because of lack of stability.

TABLE VI. EFFECT OF HOT STORAGE (78° C.) ON EXPLOSION TIME AT 134.5° C.

No.	NITRO-GLYCERIN	SALT	BEFORE HEATING		TIME OF HEATING	AFTER HEATING ^a	
			Methyl Violet at 134.5° C.	Explosion		Methyl Violet at 134.5° C.	Explosion
	%	%	Min.	Min.	Days	Min.	Min.
1	30	0.5 KNO ₃	14	130	93		73
2	30	1.5 Ba(NO ₃) ₂	14	130	94	5	101
4	40		15	300+	89	6	300+
5	30		20	300+	92	5.5	300+

^a Brown fumes showed above powders in test bottles.

Some powders which had been stored at 78° C. until brown fumes were noted in the bottles above the powders were tested by the methyl violet and explosion tests (Table VI). Even after this severe treatment the explosion test did not distinguish between good and bad powders. Powders which were obviously unstable gave satisfactory explosion tests. Such a test is unsafe to use.

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NEW GERMAN PROCESS FOR COLORING LIVING TREES. A German claims to have developed a new method for dyeing living trees to produce colored wood. Further details are on file in the Chemical Division, U. S. Department of Commerce, Washington, D. C., and may be obtained by interested American firms upon application.

Distillation Methods for Determination of Sulfur Dioxide

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THE extensive use of sulfur dioxide in preparing fruits for drying and the various governmental limitations as to the amount of sulfur dioxide permitted in foodstuffs establish a need for an accurate method for its determination. The necessity for sulfur dioxide as a preservative of the vitamins of dried fruits may in time alter the aspect of governmental control from one of maximum tolerance to one of minimum requirement, but in either case the need for control seems likely to continue. Studies in this and other laboratories on the absorption and retention of sulfur dioxide also demand a method of consistent accuracy.

Industrial control requirements demand a method affording simplicity and permitting speed without serious impairment of accuracy. In these respects the official method of the Association of Official Agricultural Chemists (2) leaves much to be desired and is not much used, even by government chemists. Moreover, the method suggested by Monier-Williams (29), although presumably more reliable, is more

IN THE DISTILLATION of sulfur dioxide from dried fruits, it was found that rapid heating generally gives more uniform results than slow heating, and that electric heaters furnish more uniform heating conditions than gas, and reduce foaming.

Other things being equal, the same normality of hydrochloric acid liberates sulfur dioxide faster or more completely than does phosphoric acid, and larger concentrations of either liberate sulfur dioxide faster or more completely than lower concentrations, within the limits tried. In this study no definite end point in the distillation was reached, and agreement between gravimetric and volumetric determinations was good when the same oxidant was used.

The use of sodium acid carbonate with either acid increases the yield of sulfur dioxide from dried fruits by about 50 p. p. m., but makes no significant change in the yield from sulfurous acid solutions.

Among the methods tried, the gravimetric Monier-Williams method gave the highest consistent recovery for sulfur dioxide from sulfurous acid solutions.

complicated and time-consuming. So many attempts have been made to simplify one or both of these methods that almost as many variations in details of methods are used as there are laboratories. In the California dried fruit industry more or less serious discrepancies have been found in the results obtained on similar materials, presumably as the result of these differences in apparatus or manipulation.

California laboratories in which dried fruits are studied have recently coöperated informally in comparing methods of determining sulfur dioxide in different portions of the same samples carefully prepared by repeated mixing and grinding at this laboratory. The results obtained by the writers in this co-operative study are fairly typical of the data obtained by most of the other workers, and together with a brief description of the methods used are given in Table I. Even the most cursory study of these data indicates that

the variations in technic have a serious effect on the results obtained, and this is borne out by the fact that the variations were just as great when different workers used what were intended to be the same methods. It seems that such variations can result only from significant differences in technic, perhaps resulting from failure to describe the methods in sufficient detail. The writers have, therefore, undertaken a study of some of the factors of possible significance.

TABLE I. SULFUR DIOXIDE DETERMINATIONS ON SAME SAMPLES BY DIFFERENT METHODS

METHOD	DETAILS	DRIED APRICOTS	DRIED PEARS	DRIED PEACHES
		P. p. m.	P. p. m.	P. p. m.
1	32-gram sample, 30 cc. tap water, 1 gram Na ₂ CO ₃ , few drops paraffin oil, 10 cc. concd. HCl, vent tube, volumetric I ₂	2006	1038	752
2	Same as 1 without Na ₂ CO ₃	..	1004	844
3	32-gram sample, 400 cc. dist. water, sample flattened and rolled between filter paper with few drops paraffin oil, 0.65 gram NaHCO ₃ , 10 cc. 50% H ₃ PO ₄ , volumetric I ₂	1636	545	413
4	Same as 3 but using 10 cc. 85% instead of 50% H ₃ PO ₄	..	588	546
5	32-gram sample, 300 cc. dist. water, 1 gram Na ₂ CO ₃ , 10 cc. concd. HCl, volumetric I ₂ with trap	1847	878	770
6	32-gram sample, 500 cc. dist. water, carbonated, heated with 20 cc. concd. HCl, reflux condenser, received in 10 cc. 3% H ₂ O ₂ , gravimetric (Monier-Williams)	1853	992	838
7	Same as 6 but not carbonated or heated before adding sample	..	983	833
8	32-gram sample, 300 cc. dist. water, 1 gram Na ₂ CO ₃ , vent tube, 10 cc. concd. HCl, received in 10 cc. 3% H ₂ O ₂ , gravimetric	1937	846	1044
9	Same as 8 but using 10 cc. 50% H ₃ PO ₄ instead of HCl	1864	855	436
10	32-gram sample, 300 cc. recently boiled dist. water, 1 gram NaHCO ₃ , 10 cc. 17% H ₃ PO ₄ distilled into Br ₂ , gravimetric (official method A. O. A. C.)	..	910	609
11	Same as 10 except using 10 cc. concd. HCl instead of H ₃ PO ₄	..	625	431

REVIEW OF LITERATURE

The literature on the determination of sulfur dioxide, sulfurous acid, or sulfites is fairly extensive. It has recently been reviewed carefully by Monier-Williams (29). This review is not intended to be complete, but is selected with respect to the principal factors bearing upon the accuracy of the distillation method.

1. SOURCE OF HEAT AND RATE OF HEATING. Zerban and Naquin (38), in 1907, considered the heating method chiefly from the standpoint of possible reactive sulfur compounds in gas which might react as sulfur dioxide, and concluded that an ordinary gas flame was safe in this respect. Black (6), in 1929, believed that rapid heating reduced flask oxidation.

2. RATE OF EVOLUTION OF SULFUR DIOXIDE AND AMOUNT OF DISTILLATE REQUIRED. Bigelow (5), in 1907, found 150 cc. of distillate adequate and stated that most of the sulfur dioxide was delivered in the first 100 cc. Zerban and Naquin (38), working with molasses, believed 800 cc. of distillate

necessary to secure all the sulfur dioxide. The official method of the Association of Official Agricultural Chemists (2) indicates that 150 cc. of distillate are adequate. May (27) recommends 200 cc. of distillate. Monier-Williams (29) recommends distillation for at least one hour, using a reflux condenser.

3. USE OF CARBON DIOXIDE OR CARBONATES.

Bigelow (5) and Zerban and Naquin (38) both recommended the use of a carbon dioxide stream, though the latter workers found it not to be of as great importance as had been supposed. Its use was recommended in the A. O. A. C. official method described in 1909 (3). Claasen (9), in 1911, found the addition of calcium carbonate in sirups to be unnecessary though giving slightly higher results. Poetschke (30), in 1913, found a carbon dioxide stream to be a satisfactory substitute for steam distillation. The A. O. A. C. method described in 1916 (1) permitted the addition of sodium acid carbonate instead of a carbon dioxide stream. Froeboese (15), in 1921, recommended the use of a stream of carbon dioxide but indicated that it aided distillation rather than prevented oxidation. Jarvinen (22), in 1925, added marble to the sample to evolve carbon dioxide. May (27) also used marble to produce carbon dioxide, allowing it to react before heating.

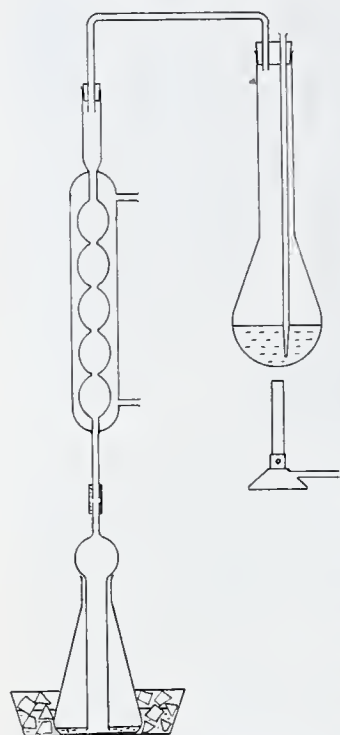


FIGURE 1. STANDARD APPARATUS WITH VENT TUBE AND RECEIVING FLASK IN ICE BATH

4. HYDROCHLORIC *vs.* PHOSPHORIC ACID IN LIBERATION OF SULFUR DIOXIDE. Gross (16), in 1925, found hydrochloric acid more rapid and convenient than phosphoric acid in liberating the sulfur dioxide from dried fruits. Hiltner (20), in 1929, confirmed the findings of Gross, whereas Roewade (32), in 1929, believed hydrochloric acid to give too high results by the liberation of additional iodine-reducing substances. Monier-Williams (29) believed hydrochloric acid was required to liberate the sulfur dioxide in dried fruits completely in one hour of distillation.

5. VOLUMETRIC *vs.* GRAVIMETRIC DETERMINATION OF SULFUR DIOXIDE. Schmidt (35), in 1904, found some precipitation of barium sulfate by substances other than sulfur dioxide in distilling dried fruits. The official method of the Association of Official Agricultural Chemists in 1909 (3) prescribed the volumetric iodine method, whereas that of 1910 (4) stipulated the gravimetric method because of the presence of non-sulfur dioxide iodine-reducing substances. Poetschke (30), working with gelatin, found the gravimetric method preferable for the same reason, as did Roewade (32), when hydrochloric acid was used in the distillation. Monier-Williams (29) found that the two methods checked very closely when cold hydrogen peroxide was used to oxidize the sulfur dioxide. Jensen (23), in 1928, pointed out slight losses of barium sulfate in the gravimetric determination.

6. SELECTIVE OXIDATION OF SULFUR DIOXIDE. The use of iodine in a volumetric determination of sulfur dioxide (3, 5, 38) is subject to certain errors pointed out by several workers (1, 4, 21). Gudeman (17), in 1909, obtained somewhat high results by collecting the distillate in a solution of sodium acid carbonate and titrating with iodine, and

Poetschke (30) found iodine preferable to bromine, as did Trotman (36), in 1924. The use of hydrogen peroxide has been suggested by several workers (8, 11, 14, 15, 18, 25, 26, 28). Monier-Williams (29) pointed out the necessity of avoiding the use of heat when this oxidant is used, and obtained satisfactory results with a number of products, using a reflux condenser, a current of carbon dioxide, and either titration or gravimetric precipitation of barium sulfate in the cold.

7. LOSS OF IODINE IN VOLUMETRIC IODINE METHOD. The danger of loss of iodine was pointed out by Bigelow (5), Vetterre (37), in 1907, Copetti (10) in 1921, and Gross (16) in 1925, who all recommended the use of traps.

8. REDUCTION OF SULFATES BY SUGARS. The work of Saillard (34) in 1913, and the seemingly different results obtained by Haaglund (19) in 1929, suggest the possibility that in the presence of sugars sulfates may be converted into intermediate reduction products reacting with iodine. This was suggested by Roewade and Lesley (33), in 1929, as a possible explanation for the higher results they obtained by the volumetric iodine method using hydrochloric instead of phosphoric acid.

9. DIRECT TITRATION OF SULFUROUS ACID BY IODINE. That the direct titration of sulfurous acid into iodine solutions is a reliable method for the determination of sulfur dioxide was indicated by Raschig (31) in 1904, and Kolthoff (24) in 1919. Brown (7), in 1910, recommended the use of glycerin in the titration as a negative catalyst in the oxidation of sulfur dioxide by dissolved oxygen. Monier-Williams (29) found close agreement between the values obtained by titration with iodine and those by sodium hydroxide after oxidation of pure sulfurous acid solutions with hydrogen peroxide.

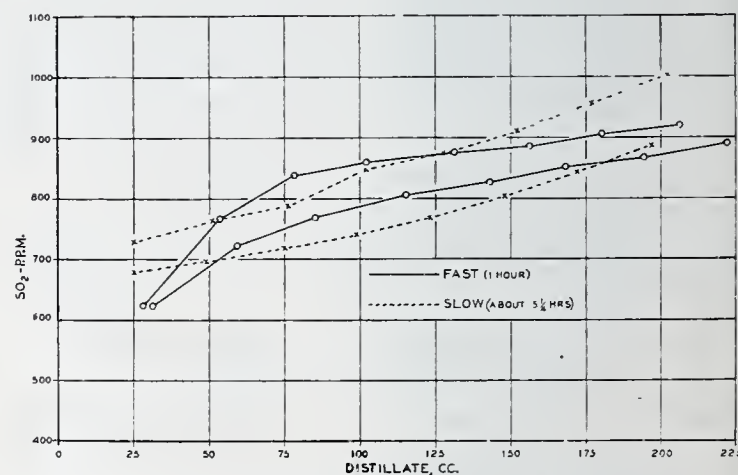


FIGURE 2. SLOW AND RAPID DISTILLATION OF SULFUR DIOXIDE FROM DRIED PEARS

10. ACCURACY OF METHODS. Bigelow (5) reported yields of sulfur dioxide ranging from 45 to 85 per cent in (dried?) fruits containing 200 to 2000 parts of sulfur dioxide per million, but it is not clear how the exact sulfur dioxide content of the fruits was known. Drake-Law (12), in 1927, concluded that the present degree of accuracy of the various methods is ± 50 p. p. m. or more. The few figures on dried fruits given by Monier-Williams (29) do not indicate such close agreement, nor does the work of Fitelson (13), in 1929, nor that shown earlier in this paper.

EXPERIMENTAL PROCEDURE

The experiments involved several types of modifications of apparatus and technic, the study of sulfurous acid and other solutions, and the examination of various samples of dried fruits.

APPARATUS. The type of equipment most commonly used in the experiments is shown in Figure 1. An 800-cc. Kjeldahl

flask is attached by two rubber stoppers and a U-shaped piece of glass tubing to an Allihn condenser. A piece of glass tubing slightly flared at the top and drawn out at the bottom to a diameter of approximately 1 mm. is inserted through a second hole in the flask stopper and reaches nearly to the bottom of the flask, so as always to be covered by the boiling liquid during distillation. This is the vent tube suggested by Hiltner (20) in 1929. The lower end of the condenser is closely joined by rubber tubing to the small end of a straight

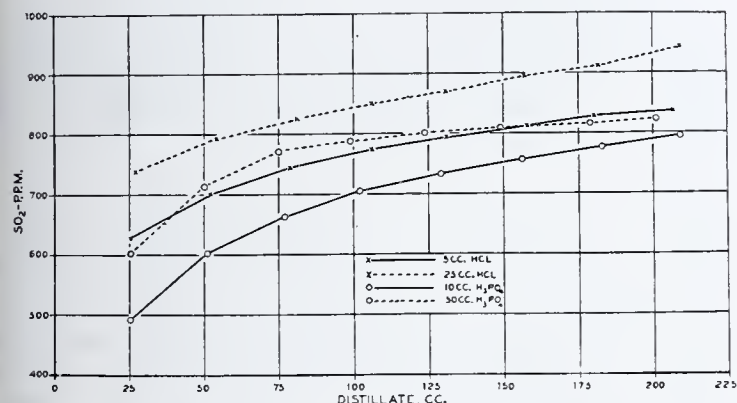


FIGURE 3. EFFECT OF KIND OF ACID ON EVOLUTION OF SULFUR DIOXIDE FROM DRIED PEARS. Concentrated hydrochloric and 20 per cent phosphoric acids; 1 gram of sodium acid carbonate in each distillation

calcium chloride tube. This acts as an adapter and dips below the surface of the oxidizing liquid in the Erlenmeyer receiving flask, the bulb of the tube fitting fairly closely in the mouth of the flask. The receiving flask stands in ice water when iodine solution is used.

This apparatus was modified in different experiments by heating with an electric heater instead of the usual gas flame, and by receiving the distillate in a graduated cylinder or a volumetric flask. Also, in some experiments the apparatus suggested by Monier-Williams (29) was used, essentially as modified by Fitelson (13).

The use of the vent tube was adopted principally because it permits the addition of acid or other solutions after the flask is connected to the condenser, and may be used for introducing a stream of carbon dioxide or other gas. It may also be closed off easily, and, all in all, affords a good deal of flexibility in operation without change of apparatus. It also eliminates danger of the liquid in the receiving flask being drawn back into the condenser or distilling flask, and prevents foaming and bumping. The oxidizing liquid in the receiving flask was 50 cc. of standardized iodine solution. In some cases bromine solution or hydrogen peroxide was used.

PROCEDURE. Unless otherwise specified, the standard procedure was to add the sample to 300 cc. of distilled (but not recently boiled) water in the flask. The flask was then connected to the condenser and receiving flask. Through the vent tube 10 cc. of 10 per cent sodium acid carbonate were added, followed within 1 to 5 minutes by 10 cc. of concentrated hydrochloric acid. Heat was applied by a gas burner, and approximately 150 cc. of distillate were obtained in about 45 minutes.

SAMPLE. When fruit was used, a 32-gram sample was always employed. On the basis of such a sample, 1 cc. of 0.1 *N* iodine or alkali used was equivalent to 100 parts of sulfur dioxide per million. For convenience of comparison when other substances or solutions were examined, the results were expressed in terms of parts per million in a 32-gram sample of fruit. Thus, adding to the distilling flask a solution of sulfurous acid containing 100 mg. of sulfur dioxide would be equivalent to and was expressed as 3125 p. p. m. Samples of fruit were prepared by mixing, grinding once

through a coarse food grinder, again mixing, and grinding through a nut-butter grinder. Solutions of sulfurous acid were prepared by passing sulfur dioxide gas from a cylinder (kindly supplied by the Virginia Smelting Company) into ordinary distilled water, unless otherwise specified. Dilutions were made as required.

RATE OF EVOLUTION OF SULFUR DIOXIDE FROM FRUIT. In studying the rate of evolution of sulfur dioxide as affected by rate of heating, source of heat, and the kind and amount of acid used, the distillate was collected in 8 fractions of approximately 25 cc. each. These fractions were collected in graduated 100-cc. cylinders standing in ice water and containing 25 cc. of 0.04 *N* iodine, and were corrected for iodine loss by blank determinations on iodine solutions allowed to stand under similar conditions for similar periods.

In one set of experiments on a single sample of dried pears in which all factors were constant except the rate of heating, greater regularity and closer agreement between duplicates were found when heating was rapid, as shown in Figure 2. After distilling 150 cc., the average values were practically the same for both fast and slow distillation, but the latter gave about 50 p. p. m. more when 200 cc. were distilled. When electric heaters were compared with gas flames by collecting the distillates in 25-cc. fractions, the values obtained on different portions of the same sample of fruit were in close agreement.

TABLE II. COMPARATIVE SULFUR DIOXIDE DETERMINATIONS ON DRIED FRUITS

FRUIT	REAGENTS ^a	VOLUMETRIC GRAVIMETRIC	
		P. p. m.	P. p. m.
Peaches	5 cc. HCl, 10 cc. NaHCO ₃	608	656
		612	619
		Av. 610	Av. 638
	25 cc. HCl, 10 cc. NaHCO ₃	668	668
		644	668
		Av. 656	Av. 668
	10 cc. H ₃ PO ₄ , 10 cc. NaHCO ₃	596	578
		578	590
		Av. 587	Av. 584
	50 cc. H ₃ PO ₄ , 10 cc. NaHCO ₃	588	588
		592	625
		Av. 590	Av. 606
(b)	5 cc. HCl, 10 cc. NaHCO ₃	1204	1207
		1240	1244
		Av. 1222	Av. 1225
	25 cc. HCl, 10 cc. NaHCO ₃	1350	1347
		1346	1344
		Av. 1348	Av. 1346
Apples	5 cc. HCl, 10 cc. NaHCO ₃	694	703
		722	712
		Av. 708	Av. 708
	25 cc. HCl, 10 cc. NaHCO ₃	782	799
	
		Av. 782	Av. 799
	10 cc. H ₃ PO ₄ , 10 cc. NaHCO ₃	606	599
		576	563
		Av. 591	Av. 581
	50 cc. H ₃ PO ₄ , 10 cc. NaHCO ₃	656	660
		686	676
		Av. 671	Av. 668
Pears	5 cc. HCl, 10 cc. NaHCO ₃	1280	1329
		1240	1261
		Av. 1260	Av. 1295
	25 cc. HCl, 10 cc. NaHCO ₃	1260	1283
		1244	1293
		Av. 1252	Av. 1288
	10 cc. H ₃ PO ₄ , 10 cc. NaHCO ₃	1200	1211
		1156	1180
		Av. 1178	Av. 1195
	50 cc. H ₃ PO ₄ , 10 cc. NaHCO ₃	1278	1293
		1252	1254
		Av. 1265	Av. 1279
Raisins	5 cc. HCl, 10 cc. NaHCO ₃	516	520
		516	494
		Av. 516	Av. 507
	25 cc. HCl, 10 cc. NaHCO ₃	576	540
		550	520
		Av. 563	Av. 530
	10 cc. H ₃ PO ₄ , 10 cc. NaHCO ₃	510	496
		512	497
		Av. 511	Av. 496
	50 cc. H ₃ PO ₄ , 10 cc. NaHCO ₃	480	466
		504	478
		Av. 492	Av. 472

^a Concentrated HCl, 20 per cent H₃PO₄, and 10 per cent NaHCO₃ used.

^b New sample.

When hydrochloric and phosphoric acids were compared in the liberation of sulfur dioxide from different portions of the same samples of dried fruits, the amounts of the acids used were such as to give approximately the same normality of acid in each pair—namely, 0.2 and 1.0 *N*—in the initial distillation mixture. Under these conditions the hydrochloric acid generally gave higher results, both by volumetric and gravimetric estimation of the sulfur dioxide evolved. The differences are significant, or possibly so in all cases except the low concentrations of acids on raisins and the high concentrations on pears. The results are shown in Table II. The results of a similar study on dried pears are shown in Figure 3.

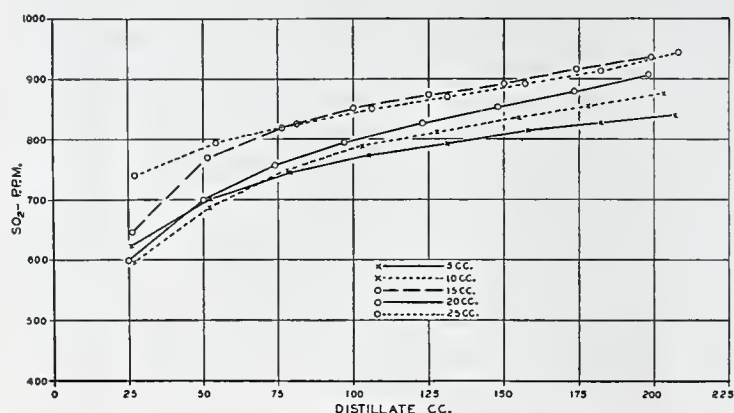


FIGURE 4. EFFECT OF VARYING AMOUNTS OF HYDROCHLORIC ACID. One gram of sodium acid carbonate in each distillation; electrically heated

Within the limits tried in the experiments just referred to, increasing the amount of acid used in the distillation generally increased the amount of sulfur dioxide recovered, as shown in Table II. This was true both of the volumetric and the gravimetric determinations, except in the hydrochloric acid comparisons on pears and the phosphoric acid comparisons on raisins. In other series of experiments the same general tendency was observed, although small increases in the amounts of acid used did not always result in higher values for sulfur dioxide, as shown in Figures 4 and 5.

When the distillates were collected in fractions, the sulfur dioxide or apparent sulfur dioxide recovered continued to increase as long as fractions were collected. This is shown in all curves in Figures 3, 4, and 5. The amount of distillate usually collected was 200 cc. when taken in fractions, or 150 cc. when taken as a whole. In one experiment, 400 cc. of distillate were collected in 25-cc. fractions, using phosphoric acid as the liberating acid for the first 275 cc. At this point, 15 cc. of concentrated hydrochloric acid were added. In the next two 25-cc. fractions, the sulfur dioxide or apparent sulfur dioxide was slightly increased, after which the rate fell off to approximately that before addition of the hydrochloric acid. The results are shown in Figure 6.

COMPARISON OF VOLUMETRIC AND GRAVIMETRIC DETERMINATION. The experiments summarized in Table II serve also to compare volumetric with gravimetric determinations using iodine as the oxidizing agent. The agreement was excellent in all cases. When sodium acid carbonate was used with either hydrochloric or phosphoric acid, the amounts of sulfur dioxide in the distillate were generally about 50 p. p. m. greater than when no sodium acid carbonate was used. The loss of iodine observed when gas was not bubbled through it and when the container was packed in ice was never equivalent to more than 5 p. p. m. Allowing the air expelled from the apparatus to pass through the iodine on boiling increased this loss to only 7 p. p. m., whereas the omission of the ice pack increased the loss to 20 p. p. m. In consideration of the above observations, no thiosulfate trap was used, but an

ice pack for the distillate receiver was adopted when iodine was used as the oxidant.

REDUCTION OF SULFATES. The possibility of reduction of sulfates in the presence of sugars and of fruit was studied by volumetric and gravimetric determinations on divided distillates. No reduction of sulfates was found, although a slight apparent additional sulfur dioxide yield was obtained in the volumetric determination on unsulfured apricots to which potassium sulfate was added. The gravimetric results on the other portions of the same distillates showed no increase in sulfur dioxide, and neither volumetric nor gravimetric determinations on sulfured peaches to which potassium sulfate or sulfuric acid had or had not been added showed any additional sulfur dioxide resulting from the addition of sulfates.

DISTILLATION OF ORGANIC SULFUR COMPOUNDS. The apparent sulfur dioxide from sulfo-proteins found by distillation of egg yolk and of onions was very small in amount. The volumetric results were slightly higher than the gravimetric on divided distillates when egg yolk was distilled; on onions, the volumetric and gravimetric results were practically the same. No appreciable reduction of sodium benzene sulfonate was found. The data from these experiments are given in Table III.

TABLE III. DECOMPOSITION OF SULFONATES AND SULFO-PROTEINS

(Based on 32-gram sample)

MATERIAL	REAGENTS	SO ₂ VOLUMETRIC	SO ₂ GRAVIMETRIC
		P. p. m.	P. p. m.
Egg yolk	10 cc. HCl, 10 cc. NaHCO ₃	36	6
		48	22
Egg yolk	10 cc. H ₃ PO ₄ , 10 cc. NaHCO ₃	44	3
		44	9
Onions	10 cc. HCl, 10 cc. NaHCO ₃	26	29
		11	30
Sodium benzene sulfonate (0.2-gram sample)	10 cc. HCl, 10 cc. NaHCO ₃	3	3
		3	6
Sodium benzene sulfonate (0.2-gram sample)	10 cc. H ₃ PO ₄ , 10 cc. NaHCO ₃	None	6
		None	6

EXPERIMENTS WITH SULFUROUS ACID SOLUTIONS

The use of sulfured fruits in the study of methods for determining sulfur dioxide is always open to two serious objections. First, the exact sulfur dioxide content of the fruit is unknown and must remain so as long as the methods studied are of questionable accuracy. Second, the sulfur dioxide in the fruit gradually disappears by volatilization or by conversion into other forms not recoverable as sulfur dioxide. For these reasons sulfurous acid solutions were used in some of these experiments. These solutions, prepared by passing sulfur dioxide gas through water, were tested for strength by direct iodine and alkali titrations, the difference being taken as representing the amount of sulfuric acid present. All stock solutions were diluted down to 1000 to 1300 p. p. m. on the usual basis before use.

COMPLETENESS OF RECOVERY OF SULFUR DIOXIDE FROM SULFUROUS ACID SOLUTIONS. Eight determinations were made using the same amounts of the same sulfurous acid solution in ordinary distilled water, the same reagents, and the same technic, receiving 150 cc. of distillate in iodine solution held in ice water. The distillation times varied from 37 to 59 minutes, averaging 50 minutes. Out of 1391 p. p. m. present, the average recovery as sulfur dioxide in the distillate was 90.2 per cent with a standard deviation of 26 p. p. m.

In another series of experiments, a number of the possible variations in procedure were tried. Omission of sodium acid carbonate was compared with the use of sodium acid car-

TABLE IV. EXPERIMENTS WITH SULFUR DIOXIDE SOLUTIONS

MATERIAL AND METHOD	Dist. Time Min.	SO ₂ Added P. p. m.	SO ₂ RECOVERED IN DISTILLATE		Volumetric		Gravimetric		OXIDIZED SO ₂ IN DISTILLATION FLASK		TOTAL SO ₂ ACCOUNTED FOR	
			P. p. m.	%	P. p. m.	%	P. p. m.	%	P. p. m.	%	P. p. m.	%
SO ₂ in dist. H ₂ O with HCl and NaHCO ₃	42	1153	1106	95.9	None	None	1106	95.9		
SO ₂ in dist. H ₂ O with CO ₂ stream; HCl and NaHCO ₃	29	1148	1086	94.6	None	None	1086	94.6		
SO ₂ in dist. H ₂ O; H ₃ PO ₄ and NaHCO ₃ into H ₂ O ₂	41	1223	951	77.8	213	25.6	1264	103.3		
SO ₂ in dist. H ₂ O; HCl and NaHCO ₃ into H ₂ O ₂	28	1250	912	72.9	888	71.1	338	27.0	1226	98.1		
SO ₂ in dist. H ₂ O; HCl but no NaHCO ₃	36	1153	1116	96.8	None	None	1116	96.8		
SO ₂ in dist. H ₂ O (29)	62	1148	1052	91.6	1134	98.9	None	None	1134	98.9		
SO ₂ in dist. H ₂ O (29); no preliminary heating	60	1148	1085	94.6	1131	98.5	None	None	1131	98.5		
SO ₂ in dist. H ₂ O (29); no preliminary heating; no guard trap	60	1250	1103	88.2	1167	93.4	None	None	1167	93.4		

bonate on distilling into iodine. Distillation into hydrogen peroxide without the use of a reflux condenser was compared with distillation into iodine and with the use of a reflux condenser. The average results are given in Table IV. Agreement between duplicate determinations was always within

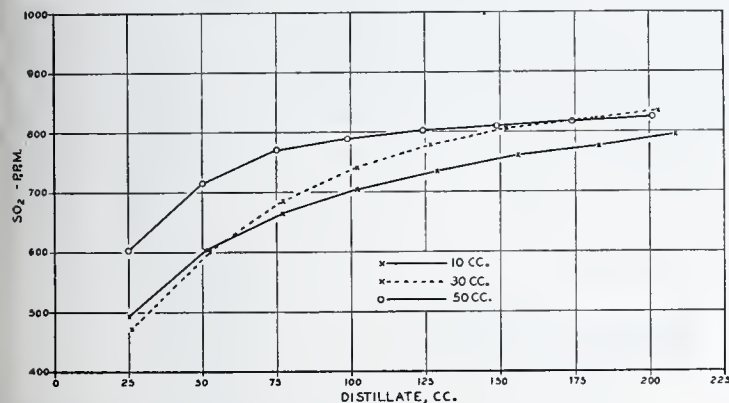


FIGURE 5. EFFECT OF VARYING AMOUNTS OF 20 PER CENT PHOSPHORIC ACID. One gram of sodium acid carbonate in each distillation; electrically heated

50 p. p. m. on the usual basis. In calculating the total sulfur dioxide accounted for, gravimetric results were used when available.

DISCUSSION OF RESULTS

The rate of heating had some influence on the rate of distillation of sulfur dioxide from dried fruits. Slow heating increased the proportion of the sulfur dioxide received in the first portions of the distillate. It also gave poor agreement between duplicate determinations. There was no essential difference between gas and electric heat provided the heating was maintained at approximately the same rate. In favor of the electric heaters, it may be said, however, that it was much easier to maintain uniformity in the boiling rate and distillation time by their use. Also, there was less tendency toward foaming in samples that gave trouble when distilled with phosphoric acid by means of gas flames, probably because the heat was distributed better over the bottoms of the distilling flasks.

When similar concentrations of hydrochloric and phosphoric acids, expressed in normality, were used for the liberation of sulfur dioxide, the former generally gave higher results. Higher concentrations of either acid usually gave higher results. On the basis of these data it seems that equally good evidence is presented that the lowest amounts of each acid used were inadequate, and that the larger amounts of hydrochloric acid are excessive. In view of the fact that the exact sulfur dioxide content of dried fruit is unknown, neither conclusion may safely be drawn. No definite end point in the distillation was located, confirming in part the findings of Zerban and Naquin (38).

No significant differences were found between gravimetric and volumetric determinations when the same oxidant and the same distillate were used. From this it is believed that the dried fruits used gave no non-sulfur iodine-reducing substances when distilled by either hydrochloric or phosphoric

acids. Discrepancies between gravimetric and volumetric results reported in the literature are believed to be due to the materials being examined, the oxidants used, or other unknown factors.

The use of sodium acid carbonate gave higher results with dried fruits but not with sulfurous acid solutions. The reason for the higher results with dried fruit is not apparent. The evolution of carbon dioxide is complete before the first 25 cc. of distillate is received. If the high results were due to a sweeping action of the carbon dioxide evolved, the increase should appear in the first fractions collected, and this was not the case. Also, since the sodium acid carbonate was present for only a minute or two before the addition of acid which immediately rendered the distillation mixture distinctly acid, the high results do not seem to be due to improved dissociation of sulfur dioxide from combination with fruit sugars as a result of alkali digestion.

The loss of iodine from the receiver during distillation without a carbon dioxide stream was kept to a very low, almost inappreciable level by packing the receiver in ice water. This method seems just as reliable and more convenient than the use of a trap, particularly if rubber stoppers are used in the latter, with the possibility of some absorption of iodine by the rubber. It must be admitted, however, that slight amounts of sulfur dioxide may escape while the apparatus is being cleared of air and carbon dioxide at the beginning of

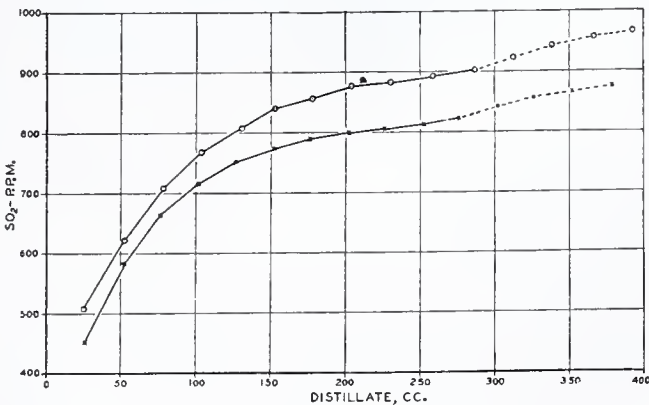


FIGURE 6. EFFECT OF LONG-CONTINUED DISTILLATION OF SULFUR DIOXIDE FROM DRIED PEARS WITH 30 CC. OF 20 PER CENT PHOSPHORIC ACID AND 1 GRAM OF SODIUM ACID CARBONATE AND A SUBSEQUENT ADDITION OF HYDROCHLORIC ACID

the distillation. When a carbon dioxide stream was used, with hydrogen peroxide as an oxidant, a trap yielded higher results and thus appears necessary.

Reduction of sulfates in the boiling mixture did not occur with either hydrochloric or phosphoric acid, or with fruits or sugars. While it is true that the volumetric results on unsulfured apricots alone and with added sulfates might indicate such a reduction, the gravimetric results do not confirm this. Also, the similar experiments with sulfured peaches do not indicate reduction in either volumetric or gravimetric results.

In the work with sulfurous acid solutions, the carbon dioxide stream appeared to have a sweeping effect rather than to prevent oxidation.

Also, in the work on sulfurous acid solutions, the high yields obtained by the Monier-Williams method are noteworthy. It appeared that in this method the use of the trap is essential in preventing mechanical loss of sulfur dioxide with the carbon dioxide stream. The preliminary heating of the acidified water, however, did not appear to affect the results appreciably.

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Analysis of Resorcin

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IN ORDER to analyze high-grade products such as resorcin, as made by present manufacturing methods, and to differentiate between samples from different sources of manufacture, it is usually necessary to give special attention to the methods of analysis and their interpretation. One of the most complete methods of analysis available is that of the U. S. Pharmacopeia, but although it serves the purpose for which it is intended, it is inadequate for technical resorcin or plant-control work.

This has emphasized the necessity for further additions to the methods of analysis—namely, an exact determination of the crystallizing point, the interpretation of crystallizing-point data, a quantitative determination of the phenol content, application of the lead acetate test commonly used for catechol, and the interpretation of this test.

DETERMINATION OF CRYSTALLIZING POINT

Two methods in common use for determination of the crystallizing point were studied, in connection with resorcin, as follows:

METHOD A. The ordinary commercial method was used. Portions of sample were introduced in a 1 by 4 inch (2.54 by 10.16 cm.) test tube and heated slightly above the melting point until the tube was nearly filled with molten sample, after which it was placed in a small bottle. The liquid was stirred with the thermometer, and excessive contact with the wall of the tube was avoided. After supercooling of about 0.1° C., crystallization proceeded and the highest temperature was taken as the crystallizing point. A precision thermometer,

A STUDY has been made of two methods for the determination of the crystallizing point of resorcin. The effect of the addition of phenol up to 6.44 per cent upon the crystallizing point of pure resorcin and the effect of the addition of water up to 0.76 per cent have been determined. Procedures have been devised for the determination of catechol, and for the determination of phenol in technical resorcin, when present.

100° to 120° C., graduated in 0.2° C. divisions and calibrated for total immersion, was used. A correction was applied for exposed stem from surface of liquid to point of reading.

METHOD B. In this method the crystallizing point was determined by extrapolation of that portion of the cooling curve representing freezing liquid to the portion representing cooling liquid. The apparatus

consisted of a wide-mouth 500-cc. Erlenmeyer flask with cork stopper, through which was fitted a stirrer and test tube 1.25 by 7.25 inches (3.17 by 18.41 cm.). Into the latter was fitted a 1 by 6 inch (2.54 by 15.24 cm.) test tube closed with a cork stopper holding a thermometer and a glass looped stirrer. The Erlenmeyer flask contained sufficient liquid petrolatum to fill it completely when hot; it was heated at the beginning of the determination to 100° to 110° C. Individual corrections were applied for exposed stem from the surface of the liquid to the middle of the stopper and from the middle of the stopper to the point of reading.

A comparison of the crystallizing points of various samples of resorcin by methods A and B were made and the results are shown in Table I and Figure 1.

TABLE I. CRYSTALLIZING POINTS BY METHODS A AND B

SAMPLE	METHOD A ° C.	METHOD B ° C.
High-grade technical	109.48	109.42
Aged and oxidized technical	108.49	108.49
Recrystallized and sublimed	109.8	109.77

Method A is apparently satisfactory for the determination of the crystallizing point of resorcin of the qualities represented.

EFFECT OF WATER. Mixtures were prepared by adding weighed amounts of water from a Lunge pipet to weighed amounts of recrystallized and sublimed resorcin. Each mixture was carefully heated and the crystallizing point determined using method A. The results given in Table II were obtained, and are plotted in Figure 2, Curve 1.

TABLE II. EFFECT OF WATER UPON CRYSTALLIZING POINT

WATER %	CRYSTALLIZING POINT ° C.
None	109.80
0.241	109.06
0.32	108.88
0.76	107.20

In these determinations, supercooling increased with increase of water content, the 0.76 per cent mixture supercooling 1.5° C.

EFFECT OF PHENOL. Thirty grams of recrystallized and sublimed resorcin were placed in a 1 by 4 inch test tube (2.54 by 10.16 cm.), a weighed amount of phenol added, and the crystallizing point determined using method A. The mixture was then melted for the additions of successive larger amounts of phenol. The results given in Table III were obtained, and are plotted in Figure 2, Curve 2.

TABLE III. EFFECT OF PHENOL UPON CRYSTALLIZING POINT

PHENOL %	CRYSTALLIZING POINT ° C.
None	109.80
0.10	109.67
0.22	109.58
0.37	109.45
0.61	109.18
1.46	108.64

Mixtures with crystallizing points below 109° C. showed increasing amounts of supercooling, a mixture with 6.4 per cent phenol, for example, supercooling 1° C.

In order to determine the effect of remelting the mixtures, a fresh mixture containing 1.61 per cent phenol was prepared. The crystallizing point corresponded to 1.60 per cent phenol on the curve.

CHANGE IN COMPOSITION OF IMPURE RESORCIN UPON DRYING. Since small amounts of water are found to have an appreciable effect upon the crystallizing point of resorcin, it appears very desirable to determine the crystallizing point after removal of the water.

Sufficient phenol was added to a sample of purified resorcin (crystallizing point, 109.66° C.) to lower the crystallizing point to 108.94° C. Water was then added to lower it to 106.48° C. The mixture was ground and dried in vacuum at 90° C. for 1 hour. The crystallizing point was then 109.48° C., showing that phenol was removed in the drying operation. This method cannot, therefore, be used for determining the crystallizing point of resorcin after drying, and since resorcin is also lost in the drying operation, it cannot be used for determining moisture in the absence of phenol.

Preliminary tests made with the purpose of drying molten resorcin with various drying agents have thus far failed to give satisfactory results. Further work will be continued on this phase of resorcin analysis, and with this accomplished it would not only be possible to determine the quality on the dry basis but also to determine the moisture content from the difference in the crystallizing points before and after drying.

DETERMINATION OF PHENOL

Since technical resorcin usually possesses a phenolic odor, whereas the pure compound is almost devoid of odor, it was considered desirable to obtain a quantitative method for the estimation of phenol.

Phenol and resorcin have very different rates of steam distillation, and therefore it was proposed to separate them by this means. A point should be reached in this distillation,

under ideal conditions, at which all of the phenol has been removed and at which resorcin distills alone at a constant rate.

From the crystallizing point data at hand for technical resorcin, it was apparent at the outset that the maximum amount of phenol involved was approximately 0.3 per cent.

Preliminary steam distillations were made using 100-gram samples of phenol-free resorcin with known amounts of phenol added. Aliquots from 500 cc. of distillate were titrated and the titrations corrected for resorcin as established by a blank determination.

It was found that the introduction of steam yielded only 10 per cent of the phenol added. When 600 cc. of the solution were boiled down without introduction of steam, 60 per cent of the phenol was obtained. Distillation from a volume of 200 cc. by heating with a flame while adding water at the same rate yielded 20 per cent. This latter experiment was repeated using a Davisson scrubber which effected a more efficient separation by lowering the blank considerably, but gave a

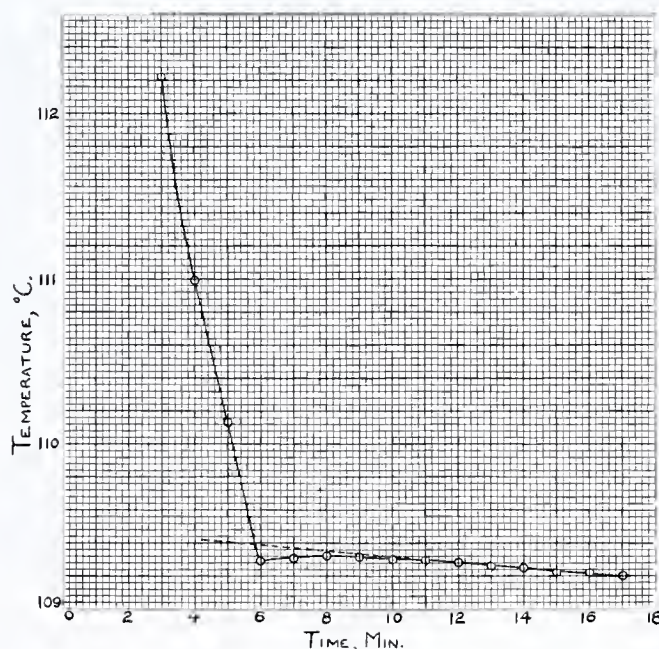


FIGURE 1. CRYSTALLIZING POINT OF RESORCIN

recovery of only 43 per cent. However, by repeating the experiment with the addition of 50 grams of sodium chloride, yields somewhat above theory were obtained. An investigation of the blank determinations resulted in variations of 0.7 cc. in the titration for five determinations, and with a more rapid rate of distillation variations of 1.1 cc. The apparatus was then modified by substituting the transite board for the wire gauze previously used, resulting in a variation of 0.15 cc. for five blank determinations.

These preliminary experiments indicated that the conditions necessary for the determination of phenol in technical resorcin by steam distillation are (1) distillation at constant volume, (2) use of sodium chloride, (3) use of a Davisson scrubber, (4) use of a large transite board under the flask to prevent irregular superheating, and (5) a concentration of 100 grams of resorcin, 50 grams of sodium chloride, and 200 cc. of water. These conditions form the basis for the final method as adopted.

The rate of distillation of phenol from known phenol-resorcin mixtures and from technical resorcin was next investigated, as was also the rate of distillation of catechol from a catechol-resorcin mixture. Catechol is a common impurity in technical resorcin. It is readily brominated and might cause interference with the phenol determination.

The data shown in Tables IV and V and on the corresponding curves were obtained under the conditions of the final

method as given below, except that in Table IV, 50-cc. aliquots of 100 cc. of distillate were brominated. Table V shows a phenol recovery by bromination of a 50-cc. aliquot of 500 cc. distillate.

The tables indicate the volume of distillate (abscissas on the curves), the amounts of 0.2 *N* bromate consumed by the total phenols in 100 cc. of distillate (ordinates on the curves), and the amounts of phenol recovered.

The resorcin used in the known mixtures was recrystallized twice from water and was odorless; the sodium chloride was of c. p. quality; the phenol was a technical product with a crystallizing point of 40° C. and phenol, 100 per cent by bromination; the catechol was a recrystallized sample melting at 104° C.

TABLE IV. RATES OF DISTILLATION BY FINAL METHOD

TOTAL VOL. OF DISTILLATE Cc.	NaBrO ₃ ADDED Cc.	Na ₂ S ₂ O ₃ USED Cc.	0.2 N NaBrO ₃ CONSUMED Cc.	RESORCIN PER 500 CC. OF DISTILLATE Gram	
A. PURE RESORCIN					
100	15.00	28.75	1.17		
200	15.00	28.60	1.24		
300	15.00	28.80	1.14	0.0376	
400	15.00	28.70	1.19		
500	15.00	28.85	1.12		
B. PURE RESORCIN WITH 0.1 PER CENT CATECHOL					
100	15.00	28.60	1.26		
200	15.00				
300	15.00	28.35	1.36		
400	15.00	28.43	1.32		
C. PURE RESORCIN WITH 0.01 PER CENT PHENOL					
100	15.00	13.08	8.85	0.0479	Added 0.1098 gram
200	15.00	20.41	5.26	0.0254	
300	15.00	24.15	3.42	0.0139	
400	15.00	26.53	2.26	0.0066	Found 0.0968 gram in first 500 cc.
500	15.00	27.70	1.68	0.0030	
600	15.00	28.13	1.47	0.0004	
700	15.00	28.40	1.34		Error, 0.013%
800	15.00	28.40	1.34		
D. TECHNICAL SAMPLE					
100	20.00	11.53	14.79		Found 0.16% in first 500 cc.
200	15.00	14.25	8.27		
300	15.00	20.73	5.10		
400	15.00	23.90	3.55		
500	15.00	26.27	2.38		
600	15.00	26.82	2.11		
700	15.00	27.75	1.66		
800	15.00	28.10	1.48		
E. PURE RESORCIN WITH 0.24 PER CENT PHENOL					
100	25.00	9.30	20.78	0.1227	Added 0.2668 gram
200	15.00	8.32	11.18	0.0625	Found 0.2440 gram in first 500 cc.
300	15.00	18.20	6.34	0.0322	
400	15.00	23.00	3.98	0.0174	Error, 0.022%
500	15.00	25.71	2.66	0.0092	
600	15.00	27.28	1.91	0.0043	Found 0.2529 gram in first 800 cc.
700	15.00	27.93	1.57	0.0023	
800	15.00	27.88	1.60	0.0023	Error, 0.014%
900	15.00	28.65	1.22		
1000	15.00	28.49	1.30		

^a Using 1.20 cc. of 0.2 *N* bromate blank.

TABLE V. PHENOL RECOVERY BY FINAL METHOD

(Pure resorcin with 0.08% phenol)

VOL. OF DISTILLATE	NaBrO ₃ Cc.	Na ₂ S ₂ O ₃ Cc.	0.2 N NaBrO ₃ CONSUMED Cc.	RECOVERY
500	15.00	23.41	3.60	Added, 0.0837 gram Found, 0.0752 gram Error, 0.008%

The tables and their corresponding curves indicate the following facts:

1. Pure resorcin distils with steam at a constant rate (Table IV-A and Figure 3, Curve 1).

2. A mixture of pure resorcin with 0.1 per cent catechol distils at a constant rate and in only slightly greater amounts than pure resorcin. Therefore, catechol does not interfere with

the estimation of phenol in resorcin by this method (Table IV-B and Figure 3, Curve 2).

3. Phenol distils at a comparatively rapid rate, a very large percentage being removed in the first 500 cc. of distillate.

4. The slopes of the curves, after 500 cc., rapidly approach zero, and the curves themselves approach the value of the blank for pure resorcin (Table IV-C, D, and E, and Figure 3, Curves 3, 4, and 5).

5. The curve for a technical sample does not differ appreciably from those obtained from mixtures of pure material, showing that the method is applicable to technical samples.

6. The average error of the determination at 500 cc. is of the order of 0.015 per cent and increases when greater amounts of phenol are being estimated.

7. There is every indication that amounts of phenol larger than 0.3 gram may be estimated by titrating an aliquot of the first 1000 cc. of distillate rather than the first 500 cc. (Table IV-E). This modification of the method would be subject to any errors involved in titrating large amounts of phenol by the specified method.

8. The recovery of phenol from a known phenol-resorcin mixture by the regular method (titration of an aliquot of 500 cc. of distillate), with an error of only 0.008 per cent, indicates finally that the method is quantitative.

IDENTIFICATION IN DISTILLATE FROM TECHNICAL RESORCIN. The steam-distillation method for the determination of phenol in resorcin obviously includes any other impurities which are volatile with steam and which absorb bromine. It may be stated, however, that all samples of technical resorcin having a phenolic odor have shown definite quantities of bromine-absorbing constituents in the distillate when subjected to the steam-distillation method.

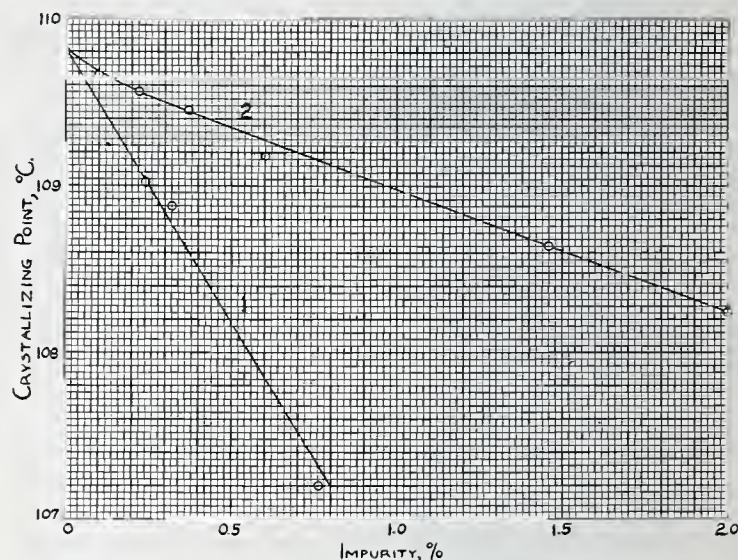


FIGURE 2. EFFECT OF IMPURITIES UPON CRYSTALLIZING POINT

(1) Resorcin and water; (2) resorcin and phenol

To 250 cc. of distillate from a sample showing 0.3 per cent phenol, 2 grams of sodium bicarbonate were added. The solution was saturated with sodium chloride and extracted twice with ether; the extract was washed and evaporated to dryness. A colorless, oily residue with a strong phenolic odor was obtained. Bromination of the residue with excess of bromine water yielded a white precipitate. This was filtered off, treated with sodium bisulfite solution, washed with water, and dried in vacuum over concentrated sulfuric acid at room temperature. It melted at 83.4° to 85.0° C. The product was extracted hot with 60 per cent alcohol and allowed to crystallize. A good yield of white crystals was obtained, with a melting point of 90.2° to 90.4° C. (theory for *s*-tribromophenol, 91° C.). The mother liquor after drying yielded crystals with a melting point of 87.3° to 89.0° C. A small amount of oily matter, which caused difficulty in thoroughly drying the crude compound, was also present.

DETAILS OF METHOD FOR DETERMINATION OF PHENOL

REAGENT. Sodium bromate solution, 0.2 *N*, 5.034 grams per liter, standardized against 0.1 *N* thiosulfate.

APPARATUS. See Figure 4.

PROCEDURE FOR TECHNICAL RESORCIN. Dry the condenser and receiver before starting the determination. Weigh 100 grams of sample into the 1-liter round-bottom flask, add 50 grams of c. p. sodium chloride, 200 cc. of water, and a few boiling chips. After connecting the apparatus, heat gently with shaking to dissolve the resorcin and salt; heat to boiling and distil at the approximate rate of one drop per second while adding water at the same rate from the graduated inlet cylinder. Maintain the volume of the distillate and that of the water added within 10 cc. Transfer each 100 cc. of distillate to a dry 500-cc. volumetric flask until exactly to volume, using only distillate to adjust this volume. Shake thoroughly and pipet a 50-cc. aliquot into a 500-cc. glass-stoppered bottle. Add 15 cc. of 0.2 *N* sodium bromate solution, about 1 gram of sodium bromide, rinse down with about 25 cc. of water, then add 5 cc. of concentrated hydrochloric acid. Stopper bottle and allow to stand 5 minutes, add about 4 grams of potassium iodide, rinse down, shake, allow to stand 5 minutes, and titrate with 0.1 *N* sodium thiosulfate solution, using starch as an internal indicator.

CALCULATION. Calculate sodium thiosulfate used to cc. of 0.2 *N*.

$$\begin{aligned} \text{Cc. 0.2 } N \text{ bromate taken} - \text{cc. 0.2 } N \text{ Na}_2\text{S}_2\text{O}_3 \text{ used} &= \text{cc. 0.2 } N \text{ bromate consumed} \\ (\text{Cc. bromate consumed} - 1.2 \text{ cc.}) \times 10 &= \text{cc. bromate consumed by phenol in entire sample} \end{aligned}$$

in which case the 1.2 cc. is the bromate required by the resorcin in 50 cc. of distillate.

$$\frac{\text{Cc. bromate consumed by phenol} \times 0.003134 \times 100}{100} = \% \text{ phenol}$$

PROCEDURE FOR U. S. P. OR HIGHER GRADES OF RESORCIN. Inasmuch as the method described is inadequate for the detection of traces of phenol in resorcin of this quality, substitute the qualitative test outlined in the U. S. P.

DETERMINATION OF CATECHOL

Catechol is frequently listed as an impurity in technical resorcin. The presence of this isomer is indicated by a qualitative lead acetate test. It was considered desirable to determine the sensitiveness of this test, and also to establish the conditions under which it might be made quantitative.

SOLUBILITY OF LEAD-CATECHOL PRECIPITATE. An excess of 4 per cent lead acetate solution, recently filtered, was added to a water solution of recrystallized catechol (m. p. 104° C.). The mixture was allowed to stand 3 hours, and was then filtered through paper, washed ten times with water, and dried for 4 hours at 70° C. A weighed sample was suspended in 100 cc. of water, agitated, and allowed to stand 24 hours, after which the lead compound was filtered on a tared Gooch crucible, dried at 70° C. for 4 hours, and weighed.

Compound taken	0.2513 gram
Compound found	0.2489 gram
Solubility	0.0160 gram per liter

The solubility of the lead-catechol compound is thus found to be sufficiently low to make a quantitative determination possible.

DETERMINATION OF CATECHOL FACTOR. In order to determine the ratio catechol to lead-catechol compound, under such conditions of precipitation as would be used in the analysis of technical resorcin containing 0.1 per cent catechol, known mixtures of recently recrystallized resorcin and catechol were prepared, using the proportions shown in Table VI. The mixtures were dissolved in 100 cc. of water, 50 cc. of 4 per cent lead acetate solution (filtered before use) were added, and the solutions allowed to stand. Coagulation and settling of the precipitates occurred within 3 hours; three of the solutions were then filtered through tared Gooch crucibles, washed with 100 cc. of water, dried at 70° C. for 4 hours, and weighed. The fourth solution was similarly treated after 24 hours' standing.

Filtrates from the samples standing 3 hours before filtering became slightly turbid upon standing 3 hours more; no precipitate settled. The filtrate from the sample standing 24 hours before filtering remained clear after standing another 24 hours.

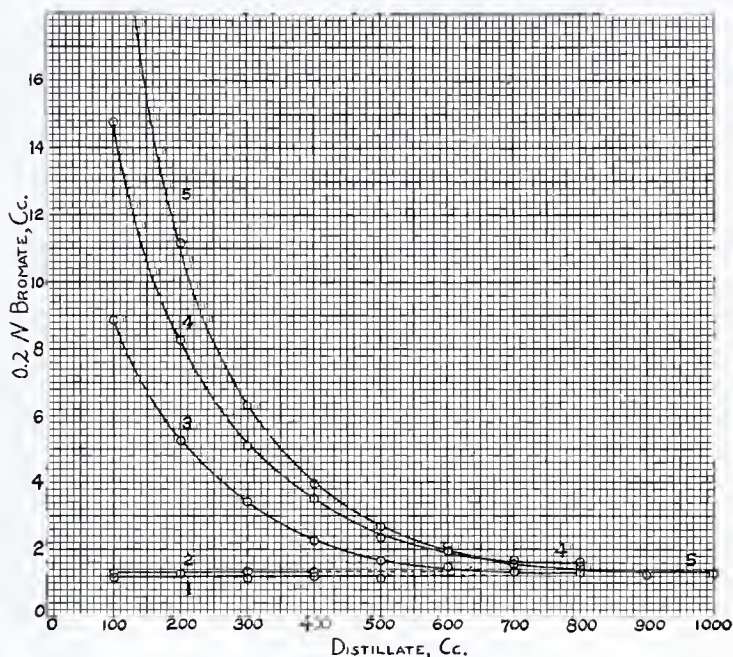


FIGURE 3. RATES OF STEAM DISTILLATION

(1) Recrystallized resorcin; (2) resorcin with 0.1 per cent catechol; (3) resorcin with 0.1 per cent phenol; (4) technical resorcin; (5) resorcin with 0.26 per cent phenol.

TABLE VI. DETERMINATION OF CATECHOL FACTOR

CATECHOL Gram	RESORCIN Gram	TIME OF STANDING Hours	LEAD-CATECHOL COMPOUND FOUND Gram	FACTOR FOUND
0.0100	10.0	3	0.0322	0.310
0.0100	10.0	3	0.0289	0.346
0.0100	10.0	3	0.0278	0.359
0.0100	10.0	24	0.0378	0.265

The mean of the first 3 values of the factor determined above is 0.339, which lies within 0.01 of the theoretical value, 0.349, calculated under the assumption that catechol and lead are united mole for mole in the lead-catechol compound. The most probable value of the factor, then, is assumed to be 0.349.

ACTION OF LEAD ACETATE UPON PURE RESORCIN. Ten grams of resorcin recently recrystallized from water were dissolved in 100 cc. of water and 50 cc. of filtered 4 per cent lead acetate were added. No turbidity and no precipitate appeared after standing 24 hours protected from fumes (H_2S or SO_3). The same concentrations were used in the determinations appearing in Table VII.

EFFECT OF LEAD ACETATE UPON RESORCIN OXIDIZED WITH HYDROGEN PEROXIDE. A sample of recently recrystallized resorcin showing no turbidity with lead acetate was treated with hydrogen peroxide, evaporated down to destroy excess of the oxidizing agent, diluted, and treated with lead acetate. A copious dark precipitate instantly formed.

EFFECT OF ACETIC ACID UPON PRECIPITATES OF LEAD COMPOUND. A few drops of acetic acid added to turbid solutions containing precipitates from any type of sample, whether produced by catechol or by oxidation products, immediately dissolved the precipitate.

CONCLUSIONS. A number of facts may be deduced from the data of the above investigation, among which are: (1) The precipitation of catechol by lead acetate under the conditions outlined above is quantitative, and is practically complete in 3 hours; catechol and lead probably unite in the

TABLE VII. ACTION OF LEAD ACETATE UPON OXIDIZED AND AGED RESORCIN AND UPON TECHNICAL AND U. S. P. RESORCIN

SAMPLE	TIME OF STANDING BEFORE FILTERING Hrs.	APPEARANCE 3 HOURS AFTER ADDITION OF LEAD ACETATE	WT. OF PPT. Gram	COMPOUNDS PPTD. BY LEAD ACETATE CALCD. AS CATECHOL %	APPEARANCE OF CLEAR FILTRATE AFTER STANDING
1. Twice recrystallized; pink in color; aged 1 week		Turbid	Not weighable		No turbidity after 24 hours
2. Three times recrystallized; brown in color; aged 5 months		Turbid; dark ppt.	Not weighable		Slight turbidity after 3 hours
3. U. S. P. resorcin; white; cryst. point, 109.8° C.	24	Slightly opalescent; no ppt. settling	Not weighable		No turbidity after 24 hours
4. U. S. P. resorcin; slightly gray; cryst. point, 109.50° C.	24	Turbid; dark ppt.	0.0126	0.043	No turbidity after 24 hours
5. Technical resorcin; lumps; inside of lumps; almost colorless	3	Very turbid; gray ppt.	0.0482	0.17	Turbid after 3 hours
6. Same as 5; outside of lumps; purple	3	Very turbid; dark brown ppt.	0.0544	0.19	Turbid after 3 hours; voluminous ppt. after 24 hours
7. Same as 5 and 6; pulverized; aged in bottle; brown	3	Very dark ppt.	0.0908	0.31	Turbid after 3 hours; voluminous ppt. after 24 hours
8. Same as 7	24	Very dark ppt.	0.1196	0.41	Slightly turbid after 24 hours
9. Technical resorcin; composite of samples; some fresh; others aged	3	Turbid; light brown ppt.	0.0221	0.07	Slightly turbid after 3 hours

proportion mole for mole; (2) lead acetate has no effect whatever upon pure, fresh resorcin; (3) the oxidation products of resorcin are partly precipitated by lead acetate in 3 hours, and more completely in 24 hours; (4) the lead acetate

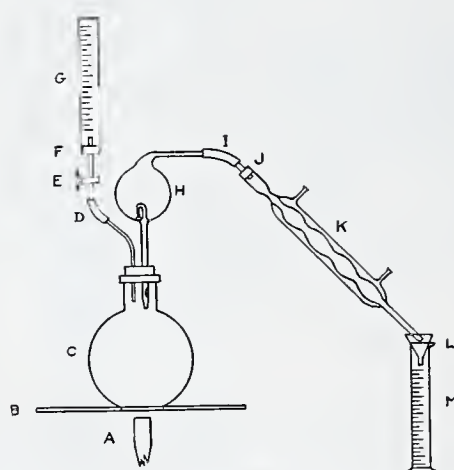


FIGURE 4. APPARATUS FOR ESTIMATION OF PHENOL IN TECHNICAL RESORCIN

- A, Meker type burner
- B, transite asbestos board
- C, 1-liter Pyrex flask
- D and I, rubber connections
- E, stopcock tube
- F and J, rubber stoppers
- G, graduated cylinder
- H, Davison scrubber
- K, Allihn condenser
- L, funnel
- M, receiver

precipitation will at all times include at least a portion of the oxidation products; therefore, the results obtained in the determination will represent maximum catechol; (5) the reagent, lead acetate, must not contain any appreciable amount of acetic acid, and this acid cannot be used to clear the turbidity of recently prepared solutions of the reagent; filtration must be used at this point; (6) the test, even when applied to highly pure grades of resorcin, is sensitive and will indicate small traces of either catechol or oxidation products by observation of the turbidity without weighing; and (7) resorcin darkens with age and oxidation; with increasing degree of oxidation a correspondingly larger amount of precipitate is obtained with lead acetate.

It is probable that lead acetate will precipitate impurities other than catechol and oxidation products of resorcin; but this matter was not investigated.

DETAILS OF METHOD FOR DETERMINATION OF CATECHOL

The method for the determination of maximum catechol, including some oxidation products, is as follows:

REAGENT. Prepare a 4 per cent solution of c. p. lead acetate, which should be turbid. Filter the reagent through No. 42 Whatman filter paper or equivalent immediately before using.

PROCEDURE FOR TECHNICAL RESORCIN. Weigh a 10-gram sample into a 400-cc. beaker, add 100 cc. of water, and stir until dissolved. Add 50 cc. of clear lead acetate reagent, stir, cover the beaker, and allow to stand 3 hours protected from fumes (SO_3 and H_2S). Filter through a tared Gooch crucible prepared with an especially thick asbestos mat. The filtrate must be perfectly clear. Wash with 100 cc. of water, dry at 70° C. for 4 hours, cool, and weigh.

$$\frac{\text{Weight of precipitate} \times 0.349 \times 100}{10} = \text{maximum \% catechol}$$

PROCEDURE FOR U. S. P. AND HIGHER GRADES OF RESORCIN. Proceed as for technical resorcin; after allowing the mixture of reagent with resorcin to stand for 3 hours, examine for opalescence, turbidity, or separation of precipitate, instead of filtering and weighing.

CHARACTERISTICS OF COMMERCIAL RESORCIN

The characteristics of high grades of resorcin of present manufacture, when determined in accordance with the methods of analysis herein described, are as follows:

TECHNICAL GRADE	
Crystallizing point	109.0° to 109.4° C.
Phenol	0.05 to 0.15%
Catechol	0.05 to 0.10%

U. S. P. GRADE	
Crystallizing point	109.5° to 109.8° C.
Phenol	None
Catechol	Not more than slight opalescence

A complete analysis of the technical grade should include bromination according to the method described in the U. S. P., examination for color, odor, and solubility. A complete analysis of the U. S. P. grade should include in addition to the usual U. S. P. tests, an examination of the color in water solution. When making comparisons, due allowance must be made for effects of age upon the material under examination.

Colorimetric Determination of Molybdenum

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THE most generally used method for the colorimetric determination of molybdenum in iron or steel was developed by Maag and McCollam (3) who combined methods previously described by the U. S. Steel Corporation (4) and by King (2). This method depends upon the extraction by ethyl ether of the brown coloration produced by the formation of molybdenum thiocyanate in a solution containing hydrochloric and sulfuric acid. The results obtained by this procedure are satisfactory, although considerable experience is required to evaporate and fume the solution successfully as directed, in order to remove the nitric acid entirely without spattering and at the same time to prevent the formation of insoluble salts by overheating.

In the following modified procedure perchloric acid is substituted for sulfuric acid, thereby eliminating entirely any tendency to spatter while removing the nitric acid, and there is moreover never any difficulty in redissolving the insoluble salts formed by boiling with this acid. Ethyl ether is also replaced as an extraction reagent by butyl acetate, an advantage in that there is no heat or pressure generated in the separatory funnel during the extraction of the molybdenum thiocyanate, a somewhat troublesome feature if ether is used for this purpose.

Nickel, chromium, vanadium, silicon, and copper do not interfere in the percentages ordinarily encountered, although it is necessary to separate the insoluble copper thiocyanate formed before estimating the molybdenum, if the copper content is much more than 0.13 per cent. It is further determined that the time designated in the following procedure for fuming with perchloric acid in order to remove the nitric acid is twice the minimum time required to complete this operation satisfactorily, and that the accuracy of the results obtained are not increased by extracting more than once with butyl acetate. The color formed does not fade and is not affected by any reasonable variation in the amount of the various reagents used.

MODIFIED METHOD

Dissolve a 0.1-gram sample of steel or iron and a standard sample of the same weight in 5 cc. of nitric acid (sp. gr. 1.13) and 5 cc. of perchloric acid (60 per cent), in 150-cc. beakers covered with raised watch glasses. The standard used may be either a steel of known molybdenum content or a standard prepared by adding to 0.1 gram of molybdenum-free steel a definite amount of standard molybdenum solution. In order to dissolve a sample of stainless steel, it is usually necessary to add to the acids used for steel 5 cc. of hydrochloric acid (sp. gr. 1.19) and 5 cc. of water. Continue to boil for 10 minutes after copious white fumes start to be given off, cool, and dissolve in 15 cc. of water. Add 5 cc. of sodium thiocyanate, agitate, and transfer to 100-cc. separatory funnels, rinsing the beakers first with 10 cc. of stannous chloride and then with 20 cc. of butyl acetate. If the sample contains less than 0.3 per cent of molybdenum, it is advisable, although not absolutely necessary, to extract with 10 rather than 20 cc. of butyl acetate, as the coloration thus produced is more readily compared with the standard.

Shake the funnels for 1 minute and discard the aqueous solutions. Add 5 cc. of sodium thiocyanate and 15 cc. of stannous chloride to the butyl acetate solutions, and again shake for 1 minute. Draw off the wash solutions and filter if an appreciable amount of insoluble copper thiocyanate is present. Transfer the butyl acetate solutions to color-com-

parison tubes, and dilute with butyl acetate saturated with sodium thiocyanate and stannous chloride until the color of the tubes is identical. The weight of molybdenum in the sample and standard is then directly proportional to the volumes. This proportionality will not hold, however, unless the solution used in matching the colors is treated as in the following directions for the preparation of the butyl acetate solution, a procedure which is necessary in order to prevent any iron present from oxidizing and the color produced by the molybdenum from fading.

SOLUTIONS

SODIUM THIOCYANATE. Dissolve 50 grams in 1000 cc. of water.

STANNOUS CHLORIDE. Heat 250 grams of stannous chloride with 200 cc. of hydrochloric acid (sp. gr. 1.19) until dissolved, and dilute without cooling with 1200 cc. of water.

BUTYL ACETATE SOLUTION. Shake 250 cc. of butyl acetate (b. p. 118° to 127° C.) in a separatory funnel with 5 cc. of sodium thiocyanate and 25 cc. of stannous chloride solution, and discard the aqueous solution. This solution must be freshly prepared each day, as it deteriorates in about 24 hours unless again saturated with the two salts.

STANDARD MOLYBDENUM SOLUTION. Heat 0.71 gram of molybdic acid (85 per cent) with 100 cc. of nitric acid (sp. gr. 1.42) and 30 cc. of hydrochloric acid (sp. gr. 1.19) until dissolved. Add 100 cc. of water, boil, cool, and dilute to 2000 cc. Determine the molybdenum content of 50 cc. of this solution as lead molybdate and calculate the concentration per cc., which should be approximately 0.0002 gram.

DETERMINATIONS

The accuracy with which molybdenum can be estimated by this method was determined in all cases by comparison with the same standard, which was prepared by adding 3 cc. of standard molybdenum solution to 0.1 gram of molybdenum-free steel. A standard prepared in this manner contained 0.000626 gram of molybdenum and was compared in all but the first two series of results with molybdenum-free steel, cast iron, or stainless steel samples prepared as the standard sample, in which, however, the molybdenum content was varied. The standard molybdenum solution was added from a 10-cc. precision buret graduated in 0.05 cc., and the colors matched against a white background.

TABLE I MOLYBDENUM DETERMINATIONS

SAMPLE	MOLYB- DENUM ADDED	MOLYBDENUM FOUND					AVERAGE
		%	%	%	%	%	
1	0.014	0.015	0.013	0.015	0.014	0.014	0.014
2	0.15	0.16	0.15	0.15	0.15	0.15	0.15
3	0.12	0.13	0.12	0.12	0.12	0.12	0.12
4	0.21	0.23	0.19	0.22	0.23	0.22	0.22
5	0.32	0.33	0.32	0.33	0.33	0.33	0.33
6	0.63	0.60	0.63	0.65	0.60	0.62	0.62
7	0.74	0.72	0.74	0.72	0.71	0.72	0.72
8	0.84	0.88	0.84	0.87	0.81	0.83	0.83
9	1.05	0.98	1.04	0.01	1.06	1.02	1.02
10	1.68	1.62	1.68	1.62	1.64	1.64	1.64
11	2.10	2.16	1.98	2.16	2.34	2.16	2.16
12	0.11	0.11	0.12	0.12	0.11	0.11	0.11
13	0.63	0.63	0.66	0.64	0.63	0.64	0.64
14	1.05	1.08	1.14	1.05	0.98	1.06	1.06
15	0.32	0.34	0.32	0.34	0.33	0.33	0.33
16	0.42	0.43	0.43	0.42	0.45	0.43	0.43
17	1.05	1.02	1.08	1.08	1.14	1.08	1.08

The series of results numbered 1 to 11 in Table I were obtained on steel samples, the first two of which were Bureau of Standards samples Nos. 30B and 72, rather than samples prepared as described. The series numbered 12 to 14 are cast iron, and the series numbered 15 to 17, stainless steel samples.

Molybdenum can be precipitated as the sulfide and weighed as lead molybdate so that the percentages thus obtained are accurate to $\pm [0.02 + (0.02 \times \text{the percentage})]$, or in other words, if molybdenum is determined in this manner, the results obtained should not deviate from the theoretical result for any definite molybdenum content by more than the value obtained by means of this equation. This value is designated as the allowable error in the following discussion, and if the results obtained deviate from the theoretical by more than this calculated error, it must be assumed that either the analyst or the method is at fault (1).

If the proposed method is to be considered as accurate as the method to which the above equation is applicable, the maximum deviations of the percentages of molybdenum determined from the theoretical percentages in Table I must be equal to or less than the allowable errors as calculated by this equation. It is evident, however, if the results are ex-

amined in this manner, that the maximum deviations for the higher percentages in this table are greater than the calculated allowable errors. Because of this fact, it must obviously be concluded that the proposed method cannot be used for a molybdenum content of more than 0.8 per cent, if it is considered necessary to determine this element as accurately as it can be determined by precipitating as the sulfide and weighing as lead molybdate.

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Determination of Total Sulfur in Gases

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THE use of gases containing a minimum amount of organic sulfur is essential for the successful operation of a number of industrial processes. In the development of methods for the removal of organic sulfur from gases it is prerequisite that a method be available for the determination of percentages of organic sulfur of the magnitude of one grain per 100 cubic feet, 0.008 per cent by volume.

The methods commonly used for official gas testing are those in which the gas is burned with oxygen or air, the resulting sulfur dioxide being converted to sulfuric acid and the final product determined by gravimetric or volumetric means. Dennis (2) gives a bibliography including many of these and describes the three methods recommended by the Bureau of Standards (1)—i. e., the Referees, the Hinman-Jenkins, and their modification of the Drehschmidt (3). The Bureau of Standards (1) states that each has its particular advantage and that it is not possible to combine all of these in any composite apparatus, nor is any of the three superior to the other two for all purposes. Further, it is noteworthy that none of the authors has demonstrated the reliability of his method on the basis of the analysis of gases of known sulfur content.

The purpose of this paper is to present a method which, in addition to its demonstrated accuracy, possesses a number of advantages over the standard methods in use in the industry.

MATERIALS USED

Carbon bisulfide, high grade c. p., showed no residue upon distillation and boiled within a narrow range (b. p. 46.0° to 46.2° C.). Ethyl sulfide, Eastman Kodak Co., had

AN IMPROVED method for the determination of the total sulfur content of gases is presented. A study of its reliability based upon analysis of a series of synthetic mixtures containing a number of types of sulfur compounds in concentrations found in refinery gases, and also covering a wide range of B. t. u. values, showed a mean error of 0.03 per cent, corresponding to a mean error of 2.4 per cent on a basis of the actual sulfur content of the gas. Analysis by two operators on similar equipments analyzing samples of the same gas agree within 1 per cent of the actual sulfur content.

An analysis by the procedure described required from 1 to 100 liters of gas. Combustion may be completed in 1 to 4 hours, and the sulfur in the absorbent medium is determined gravimetrically as barium sulfate.

a boiling point of 92° to 93° C., and thiophene (synthetic), Eastman Kodak Co., 83° to 85° C. Analysis in this laboratory of a sample of sodium carbonate from Eimer and Amend labeled "special purified, sulfur free," showed zero sulfur.

The gases ethane, propane, and butane were available in 3-pound cylinders. Samples of these gases when burned by the combustion apparatus described in this paper showed zero sulfur. Oxygen, nitrogen, and hydrogen were obtained from the Air Reduction Company. Samples of these gases burned with hydrogen in the combustion apparatus also showed zero sulfur.

The various sulfur compounds were diluted by means of a specially purified benzene which showed 0.015 per cent sulfur by the lamp method (correction was applied for this sulfur in all determinations in which it was used).

APPARATUS

The complete set-up for the proposed modified Drehschmidt apparatus is shown in Figure 1. It consists of the flowmeters, etc., which are used for measuring the volumes of the gases used in the combustion process; the combustion apparatus, *E*, shown in detail in Figure 2, in which the gases are burned; and the Milligan absorption bottles, *L*, which contain the absorption solution through which the products of combustion are bubbled. *A* is a 500-cc. round-bottom flask with stopper as shown, and *B* is an ordinary wash bottle whose inlet tube has been severed midway; these are expansion bulbs provided to even out fluctuations in pressure.

The combustion apparatus (Figure 2) consists of the chamber in which the combustion takes place and the con-

denser, *C*, to condense the water vapor formed in the combustion and to cool the gases so as to render the absorption of the oxides of sulfur more efficient. The gas jet, *T*, is sealed into tube *D* with the relative positions of the tip of the jet and the primary oxygen inlet as shown in the diagram. The capillary tube and stopcock *S*₂ permit fine control of the primary oxygen and thus give a steady flame which is essential to the successful operation of the apparatus. The ground-glass joints are interchangeable and require no stopcock grease. The gas mixture is ignited by means of a spark produced at the terminals of platinum leads, *F*, by means of an induction coil of the ordinary Ford type. The spark is turned off and on by means of a switch not shown in the diagram. The ground-glass joints on the Milligan bottles do not require stopcock grease; a film of water, obtained by wetting both members of the joint before closing the bottles for use, serves to maintain a tight joint. The mercury manometer (*T*, Figure 1) measures the pressure at which the gas sample is introduced into the apparatus.

The gases oxygen and nitrogen are supplied from the original pressure containers fitted with Hoke valves. The gas to be burned is run either directly from its source (if under pressure) and its pressure controlled by a needle valve, or from its container—e. g., a 20-liter bottle—by water displacement at constant pressure. If hydrogen sulfide or other sulfur compounds soluble in water are present, it is necessary to determine these in another sample.

The entire apparatus including the combustion tube (*D*, Figure 2) is constructed of Pyrex glass.

OPERATION OF APPARATUS

The combustion apparatus is washed with distilled water by removing ground-glass stopper *K* and draining through outlet *S*₃. Stopcock *S*₁ is kept closed during this washing and stopper *K* is replaced after drying. The absorption bottles are washed with distilled water and filled with 5 per cent sodium carbonate solution containing 2 per cent bromine. Stock solutions should be well stoppered to prevent contamination with sulfur compounds from the atmosphere. The absorption train is connected in the manner shown in Figure 1, making sure that all glass connections are made butt to butt and that pure sulfur-free gum-rubber tubing is used for all connections. Water is circulated through condenser *C*. Stopcocks *S*₂ and *S*₃ are closed and *S*₁ is opened.

Oxygen, 50 to 100 per cent in excess of the theoretical amount required for the combustion of the gas concerned, is allowed to flow through the apparatus at the rate of approximately 0.05 cubic foot per minute. Nitrogen is then admitted at the rate of about 0.02 cubic foot per minute. When the apparatus is flushed out with the oxygen-nitrogen mixture, the spark is turned on, and the gas to be burned is introduced into the apparatus at the rate of 0.005 to 0.01 cubic foot per minute by proper control of the Hoke valve. Ignition takes place in a few seconds without explosion or back-fire, and the mixture is allowed to burn steadily for 15 seconds before the spark is turned off. At this point, the flame normally appears pale blue, topped and streaked with yellow. If the flame is entirely yellow and smoky, insufficient oxygen is being used and the volume should be increased with a proportionate increase in the volume of nitrogen. Primary oxygen is introduced by opening stopcock *S*₂ gradually until the yellow portion of the flame disappears and the flame burns with a clearly defined inner and outer cone. Too much primary oxygen should not be used since it produces an unstable flame. This is recognized by its tendency to be sucked down into the tube (*D*, Figure 2), whereupon back-fire may result. A steady purplish to blue Bunsen-like flame may always be obtained by proper regulation of the

primary oxygen and adjustment of the supply of nitrogen. If the flame should be extinguished for any reason whatever when the spark is turned off, the flow of the combustible gas must be stopped immediately. The apparatus is flushed out with the oxygen-nitrogen mixture for about 2 minutes, the spark turned on, and the ignition started again in the manner described above. *Serious explosion may occur if this simple precaution of flushing out the apparatus is not followed.*

When the flame is steady, it is only necessary to keep the gas flow constant and observe that the gas always burns with a Bunsen-like flame. When sufficient gas has been burned (from 1 to 100 liters), the combustion is stopped by first closing stopcock *S*₂ and then shutting off the gas flow at the Hoke valve, Figure 1. The apparatus is flushed out with the oxygen-nitrogen mixture for about 2 minutes before shutting off this mixture.

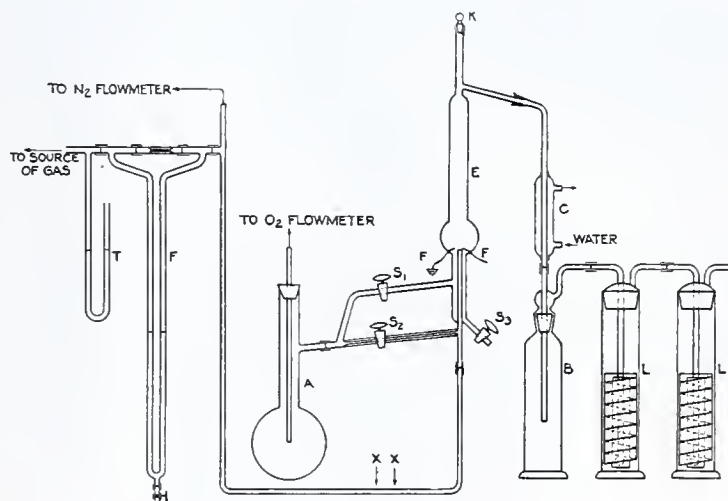


FIGURE 1. APPARATUS ASSEMBLED FOR DETERMINATION

The solutions in the Milligan bottles are transferred to a common container, and each piece is rinsed three times with 50-cc. portions of distilled water. The stopper *K* is removed from the combustion apparatus which has cooled down in the meantime and, with expansion bulb *B* (Figure 1) still attached, the combustion chamber is washed with 50-cc. portions of distilled water, allowing some of the water to run through the exit line into bulb *B*. This is repeated and finally the contents of *B* are run into the common container and then *B* is rinsed twice. The apparatus is now ready for another combustion.

The collected washings, which average about 800 cc., are now analyzed for sulfur gravimetrically as barium sulfate. The weight of barium sulfate obtained is corrected by a blank which must be run on all reagents and distilled water. The sulfur in the gas is calculated by means of the following equation:

$$w \times 15.4 \times 0.1374 \times \frac{100}{F \times p} \times \frac{P + S}{760} \times \frac{273}{T + 273} = \text{grains } S \text{ per 100 cu. ft.}$$

where

- w* = weight of barium sulfate in grams
- T* = atmospheric temperature during analysis
- p* = volume of gas per minute from flowmeter reading
- F* = time in minutes required to burn gas
- P* = barometric pressure
- S* = pressure on gas as indicated by manometer *T* (Figure 1)

DETERMINATION OF SULFUR AS BARIUM SULFATE

To the collected washings, which consist of a solution of sodium carbonate and soluble sulfur compounds, 1 or 2 cc. of liquid bromine are added, and the liquid is concentrated upon a hot plate to about one-half of its original volume.

TABLE I. SYNTHETIC ORGANIC SULFUR GASEOUS COMBUSTIONS

Run	29	30	42	44	46	50	52
Sulfur sought, grams	0.0411	0.0988	0.0306	0.0132	0.0264	0.011	0.0004
Sulfur found, grams	0.0418	0.0966	0.0310	0.0139	0.0255	0.011	0.0004
Sulfur sought, grains/100 cu. ft.	63.3	152.0	47.1	20.3	40.6	1.7	0.6
Sulfur found, grains/100 cu. ft.	64.3	148.8	47.7	21.4	39.2	1.7	0.6
Deviation from sulfur sought, %	1.7	2.2	1.3	5.4	3.4	0.0	0.0
Sulfur sought, %	3.08	3.08	1.05	1.05	0.93	0.027	0.027
Sulfur found, %	3.12	3.01	1.06	1.11	0.90	0.027	0.027
Error, %	0.04	0.07	0.01	0.06	0.03	0.0	0.0
Type of sulfur compound	CS ₂	CS ₂	(C ₂ H ₅) ₂ S	(C ₂ H ₅) ₂ S	C ₄ H ₄ S	C ₄ H ₄ S	C ₄ H ₄ S
Diluent gas ^a	P	M	M	P	H	E	B

^a M, methane; E, ethane; P, propane; H, hydrogen; B, butane.

The alkaline hypobromite solution containing the completely oxidized sulfur compounds is now rendered acid with concentrated hydrochloric acid and evaporated to dryness, whereupon all bromine is liberated. Any silicon dioxide resulting from the action of alkali upon the glass beaker is thereby completely dehydrated. The residue, which is now free from excess hydrochloric acid, is cooled, taken up with 200 cc. of water, and filtered through a quantitative filter

products of combustion were determined gravimetrically as barium sulfate.

The procedure consisted of making up stock benzene solutions of the organic sulfur compounds, carbon bisulfide, ethyl sulfide, and thiophene, in concentrations of 0.03 to 3 per cent of sulfur. From 1 to 3 grams of the stock solutions were introduced in the previously weighed empty bubbler container shown in Figure 3. The stopcocks were closed, and the exit tubes were blown dry by means of air and again weighed to ascertain the weight of sample in the container. The container was then connected at points marked XX (Figure 1). A pure hydrocarbon gas or hydrogen was run from its reservoir, a 5-gallon bottle, by water displacement at constant pressure and bubbled through the benzene-organic sulfur solution at the rate of 0.015 cubic foot per minute until all of the liquid was evaporated and burned in the combustion apparatus with the necessary oxygen and nitrogen. Additional hydrocarbon gas or hydrogen was passed through for 5 minutes to clear the lines of the synthetic sulfur mixture.

The results on a number of runs using the several sulfur compounds combusted are given in Table I.

DISCUSSION

The method described in this paper permits the determination of total sulfur in the gas when the sample may be taken directly from its source under pressure. When it is necessary to displace the sample from its container by water displacement, any sulfur compounds present in the gas which are soluble in water—e. g., hydrogen sulfide—must be de-

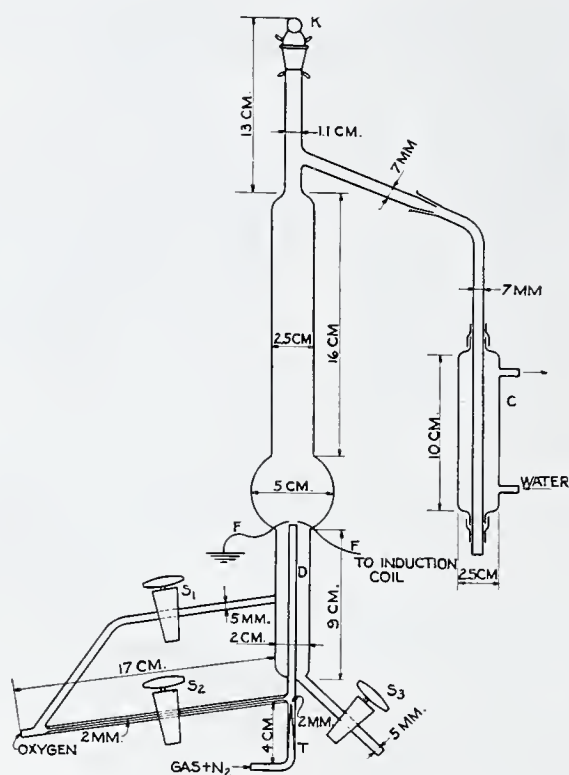


FIGURE 2. DETAILS OF COMBUSTION APPARATUS

paper to remove the silicon dioxide. The filtrate is diluted with water to about 250 cc., just acidified with hydrochloric acid, using methyl orange to indicate the acidity, and brought to boiling. At this time 25 cc. of a filtered 10 per cent barium chloride solution are added drop by drop and the whole volume stirred vigorously. The liquid containing the barium sulfate is again returned to the hot plate and brought to the boiling point. Finally, it is allowed to remain on the hot plate at gentle heat for 12 hours. If the amount of barium sulfate present is less than 4 mg., it is advisable to use a micro Gooch crucible and a microbalance in determining the amount present. The barium sulfate is filtered through the prepared Gooch crucible, washed, dried in the oven, ignited, and weighed.

EXPERIMENTAL PROCEDURE AND RESULTS

In determining the reliability of the proposed apparatus using the procedure described below, a number of synthetic gaseous mixtures containing known percentages of organic sulfur were burned in the apparatus, and the sulfur in the

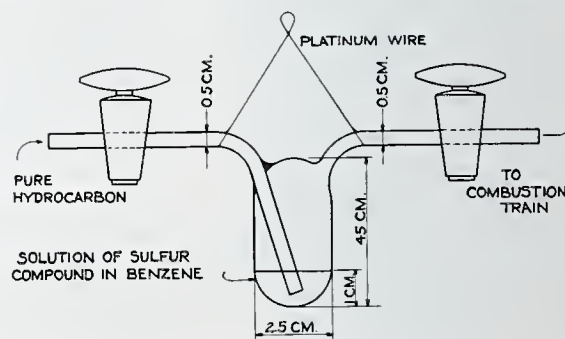


FIGURE 3. BUBBLER USED IN PREPARATION OF SYNTHETIC MIXTURES

termined first by methods which are quite well standardized. Since, however, where small quantities of total sulfur are concerned, hydrogen sulfide is either absent or has been removed from the original gas, this is seldom necessary.

In the investigation of the applicability of this method, the compounds thiophene, ethyl sulfide, and carbon bisulfide were chosen as representative of those sulfur compounds which may occur in refinery gases and also as compounds representing various degrees of stability.

From a summary of the data in Table II, it is apparent that the mean error by the proposed method is only 0.03 per cent and the mean deviation from the sulfur sought is 2.4 per cent.

The reproducibility of results by the proposed method is illustrated by the following tabulation, obtained by two different operators burning the same type of gas at approximately the same rate on two similar equipments:

APPARATUS	SULFUR FOUND
A	9.7 grains/100 cu. ft.
B	9.6 grains/100 cu. ft.

In the case of most of the synthetic mixtures, a hydrocarbon was used as the diluent for the sulfur compound. To demonstrate that the method is applicable to gases of low B. t. u. value, several synthetic samples were burned using hydrogen as the diluent. It is apparent from Table I that equal reliability was obtained for the range of B. t. u. value of the gases investigated.

TABLE II. SUMMARY OF ACCURACY DATA

Substance burned	CARBON DISULFIDE	ETHYL SULFIDE	THIO- PHENE	MEAN ^a
Number of runs	2	2	3	7
Maximum error, %	0.07	0.06	0.03	0.05
Minimum error, %	0.04	0.01	0.00	0.01
Maximum deviation, %	2.2	5.4	3.4	3.9
Minimum deviation, %	1.7	1.3	0.0	0.9
Mean error, %	0.06	0.04	0.02	0.03
Mean deviation, %	2.0	3.4	1.7	2.4

^a Based upon the weighted average of the three previous columns.

Analysis of sulfur by the method described requires from 1 to 100 liters of gas. Combustion may be completed in 1 to 4 hours, and the sulfur in the absorbent medium is determined gravimetrically as barium sulfate.

The improvements which the proposed method offers over the previously suggested modifications of the original Drehschmidt method (3), in particular that of the Bureau of Standards, may be enumerated as follows:

1. Demonstrated accuracy and reliability on the basis of the analysis of gases of known organic sulfur content.

2. Elimination of rubber and cork stoppers, wax, and de Khotinsky cement by the use of all Pyrex-glass construction with ground-glass joints, stoppers, and stopcocks.

3. Addition of a condenser to cool the products of combustion, thereby increasing the efficiency of their absorption by the absorption solution.

4. Use of platinum-to-glass sealed leads for the spark gap, instead of copper- or nickel-platinum leads, eliminating the reaction of the sulfur dioxide with the copper or nickel.

5. Use of a spherical combustion chamber to prevent impingement of the flame and subsequent collapse of the glass walls.

6. Entering of gases into the apparatus at pressures above atmospheric and thus eliminating suction required in other methods.

7. Use of pure oxygen and nitrogen instead of air for the combustion, thus eliminating possible contamination of gas burned with sulfur that may be present in the air.

8. Elimination of dangers due to explosions.

9. Adaptability of the method to gases over a considerable range of B. t. u. value.

10. Use of burner constructed of Pyrex sealed directly to and being a part of the combustion chamber, thereby eliminating quartz or porcelain. Since the latter required rubber seals, this source of contamination is obviated. The Pyrex burning tube has shown no tendency to melt and close up after being in use for several months. In fact, a crystalline ring of silicon dioxide forms at the tip and is heat-resistant.

In the procedure described, the sulfur is determined gravimetrically as barium sulfate. When the sulfur content of gas is high, the sulfur may be determined with sufficient accuracy by iodine titration of the collected washings or by means of a turbidimeter. These methods, however, have not been found satisfactory when the sulfur content of the gas is less than 2 and 3 grains per 100 cubic feet.

LITERATURE CITED

- (1) Bur. Standards, *Circ.* 48, 129 (1916).
- (2) Dennis and Nichols, "Gas Analysis," p. 351, Macmillan, 1929.
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RECEIVED August 26, 1931.

A Bicycle-Chain Stirrer

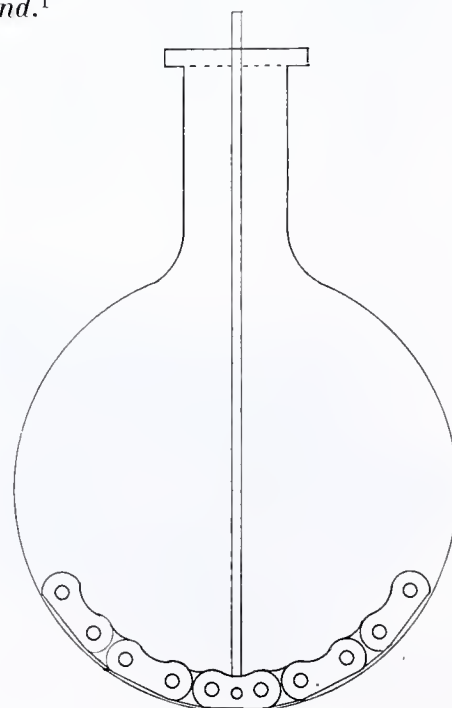
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A STIRRER has been devised which will lie close to the wall of a flask and when turned will scrape the wall clean. It is made from a short piece of ordinary bicycle chain. A hole is drilled through the middle link and an iron rod is chosen which just fits into the link. A hole similar to the one in the link is drilled through the rod near one end. The chain is fastened to the rod with a small pin in such a way that it can be inserted into the flask so that the smooth side of the chain lies against the glass. The rod may be passed through a mercury seal if so desired.

The advantages of such a stirrer are: (1) that it can be inserted and removed from the flask very easily; (2) that it fits perfectly the wall of the flask whether with round or flat bottom; (3) that it can be used (within limits) in different sized flasks without varying the length of the chain, since in small flasks the extra links simply double back; and (4) that it functions smoothly even though the rod is out of line with respect to the axis of the flask.

It is recommended for use in any case where it is desired to keep a solid worked free from the wall of a flask and an

ordinary stirrer fails to do so. Of course, it cannot be used in cases where iron will interfere with the desired reaction. The author has used it successfully in a vapor-phase reaction between magnesium and chlorobenzene in the absence of a solvent.



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A BICYCLE-CHAIN STIRRER

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Rapid Exposure Tests on Finishes

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ACCCELERATED testing cabinets have been constructed at this laboratory and experimented with for several years. These cabinets include quartz-tube mercury-vapor lamps, Weather-O-Meter carbon-arc lamps, and high-amperage carbon-arc lamps. The lamps have usually been placed in metal cabinets of sufficient size to hold from 20 to 50 test panels 5 by 10 inches (12.7 by 25.4 cm.) in size, and provision is made for spraying the coated surfaces with water from time to time. As a result of several hundred tests it is believed that such cabinets may prove useful in securing comparative results on such products as lacquers and some types of enamels. Results on varnishes do not always check with exterior exposure tests. Oil paints usually show very rapid chalking, but it has been difficult to secure such defects

as checking, alligatoring, and scaling which are shown on exterior surfaces under practical conditions. For this reason, it is the writer's opinion that accelerated cabinets have only a limited field of use, and that actual exposure tests should accompany all cabinet tests.

Because of the varying climatic conditions in most parts of the country during the different seasons of the year, the exposure of panels out of doors for quick breakdown tests (three months or less) is not practical at all seasons, as the same results would not be obtained in the winter as in the summer months. For this reason, some manufacturers have found it advisable to restrict their exposure tests to a period extending from May to October, a period of the year when the sunlight is most intense. During the balance of the year

it is probably desirable for manufacturers to have their tests exposed in a section of the country where climatic conditions do not vary greatly. The southern Florida peninsula, where there is sunshine for 359 days of the year, affords an ideal place for such work. Moreover, the atmosphere at that point is practically free from smoke. A site may be selected for test within a mile of the ocean, and racks erected. The panels should preferably be exposed at an angle of 45 degrees to the vertical, facing south, although one observer has indicated that exposures to the east, west, or south all weather with about the same degree of rapidity because of the intense sunlight conditions. Exposure tests on house paints, enamels, varnishes, sign colors, automobile finishes, and other industrial products may be made on such racks. As a rule, a period of three months will give some information on many types of finishes. A period of four weeks is usually sufficient to break down inferior varnishes or coatings which are not properly designed. An exposure for one year will often afford some information on the durability of oil paints.

RACKS FOR OUTDOOR TESTS

From time to time manufacturers desire tests on marine compositions which are to be employed on the exterior skin of ships, especially at the water line where the most severe service is shown. For instance, at the water line of navy vessels, a paint known as "boot-topping" is employed. This paint is subjected to alternate exposure to salt water and air. Such coatings often break down very rapidly, and to date but few products have proved entirely satisfactory for the purpose. For this reason, boot-toppings must be renewed frequently, especially on battleships where a trim appearance and freedom from corrosion must be maintained. Where tests of this sort are contemplated, it is suggested that racks be built in the ocean at a point near the shore, where they will be available for inspection. Such racks are shown in Figure 1. At low tide the water recedes to such an extent that the panels may be inspected if the observer will wade out to his

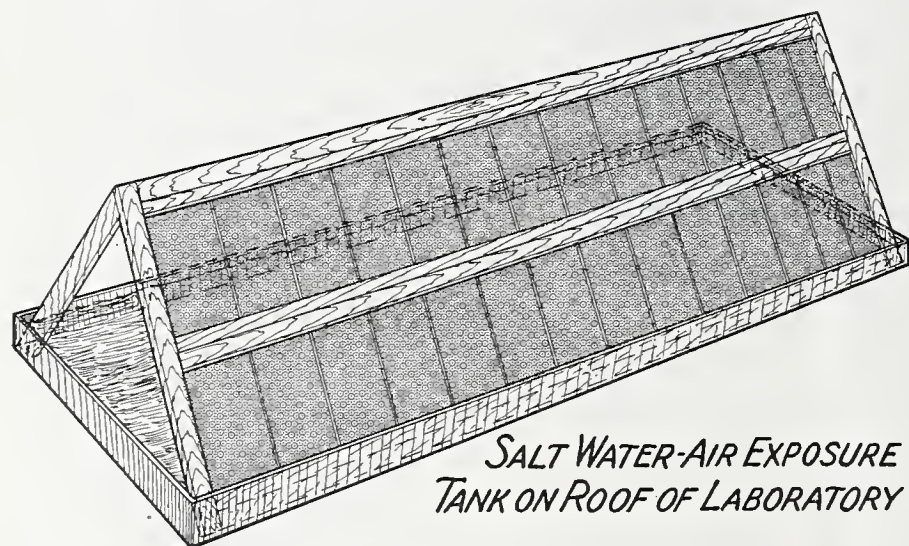
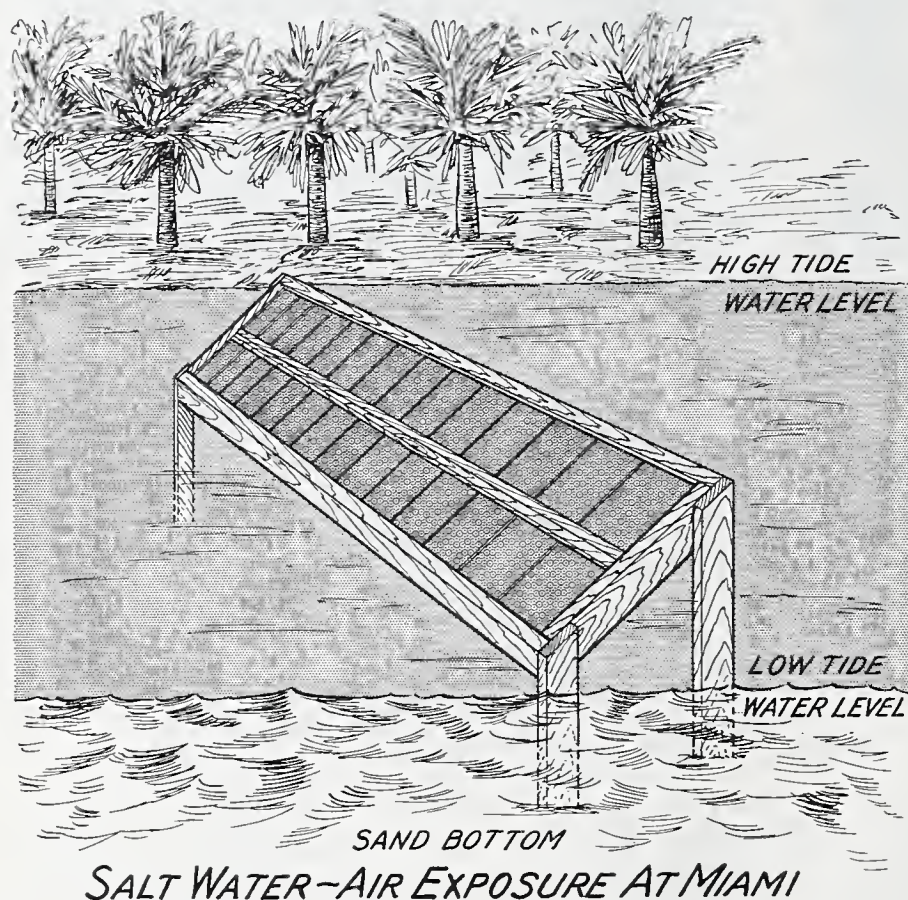


FIGURE 1

knees. During the daytime the tests receive sun exposure, and at high tide they are completely covered by sea water. Practically all coatings are to some extent permeable to salt water. The water going through the coating causes rapid corrosion of the underlying metal or contraction and discoloration defects on wood. During the drying-out period, the water is eliminated, but part of the salt contained in the water may be retained in the film and cause disintegration.

In making tests of varnish under any of the conditions referred to above, it is highly important to take into consideration the length of oil and the percentage of non-volatile matter. Thus, for instance, a varnish which contains 60 per cent of non-volatile matter will naturally form a very much thicker film than one which may be of the same viscosity but which contains only 40 per cent of non-volatile matter. Thickness of film is a vital factor in the durability of a coating material. It is usually desirable in making comparisons to determine the thickness of film after application of the finishing system by removing a portion of the coated surface about 1 mm. square, and then using an instrument such as the Ames dial micrometer on the abraded surface and on the unabraded surface. The film should preferably be at least 30 microns in thickness to give good results.

LABORATORY TESTS

For manufacturers who have not made arrangements for the exposure of tests in Florida, and who prefer to have their tests under their own supervision so that daily inspections can be made, it is suggested that an apparatus such as is shown in the lower part of Figure 1 be experimented with. This apparatus has been recently designed by the writer and has been in service during the past three months in conducting tests on the roof of the laboratory.

In considering the results outlined in the Washington roof salt-water test, it is apparent that one flow coat of coating material is entirely insufficient to produce a film which will withstand such a test for any extended period of time. On the right side of Table II referring to these tests, the results obtained on panels coated with three brush coats of coating materials are more in line with those which are obtained by actual exposure to the air. Figure 2 shows the rusted and whitened surfaces of the panels after ten days' exposure.

In these tests, the low-cook phenolic and modified phenolic resin-long oil varnishes gave generally satisfactory results as compared to the other coatings. Rapid failure was shown by sulfur-treated varnishes, lead tungate liquids, boiled linseed oil, gloss oil, and a rubber varnish which has been recently advocated as a water-resistant product. It must be pointed out that to date insufficient tests have been made with this type of exposure test to warrant any general conclusions. However, because of the speed with which results may be obtained, it is suggested for experimentation on the part of other investigators.



FIGURE 2. RESULTS OF WASHINGTON ROOF SALT WATER-AIR TEST AFTER 10 DAYS' EXPOSURE

In making water exposures of varnishes which are designed for use upon yachts, the writer has employed oak panels at Miami, and prefers them to steel, as the rusting of the steel will greatly affect the durability of the varnish and give results which are not comparable to those obtained on wood. The writer has used oak panels 12 by 18 inches (30.4 by 45.7

TABLE I. SALT WATER-AIR TEST IN OCEAN AT MIAMI

(Inspection at end of 6 weeks' exposure)

No.	VARNISH	STEEL 2 brush coats	WOOD 3 brush coats
958	Phenolic resin 2540 low-cook tung oil varnish, 44 gal. length; purchased	Failed; 50% rusted	O. K. ^a
959	Modified phenolic resin 2260 low-cook tung oil varnish, 44 gal. length; purchased	Failed; 60% rusted	O. K. ^a
962	Phenolic resin 2540 low-cook tung oil varnish, 44 gal. length; made in laboratory	Failed; 20% rusted	O. K. ^a
963	Modified phenolic resin 2260 low-cook tung oil varnish, 44 gal. length; made in laboratory	Failed; 50% rusted	O. K. ^a
964	Old-type slow-drying 30 gal. ester gum tung oil varnish; 600° cook	Failed; 100% rusted ^b	Bad checking; removed from test
966	25 gal. tung oil-synthetic ester No. 1 varnish containing 0.01% sulfur; cooked at 600° F. (315° C.)	Failed; 100% rusted ^b	Bad checking; removed from test
967	44 gal. synthetic ester No. 1 tung oil varnish containing 0.05% sulfur; low cook	Failed; 80% rusted	Bad checking; removed from test
968	44 gal. ester gum-tung oil varnish containing 0.1% sulfur; low cook	Failed; 100% rusted	Bad checking; removed from test
969	Lacquer made with equal parts nitrocellulose and glycerol ester PRX	Failed; 30% rusted	O. K.

^a Complete breakdown and covered with rust in one month.

^b High gloss on wood panels at end of one month.

Note. At end of ten weeks, panels 958, 959, 962, and 963 had medium gloss. First three showed some slight grain erosion but were in fairly good condition, especially 962. Some mildew and water-spotting of the wood was shown on 963 and 969.

TABLE II. SALT WATER-AIR TEST ON ROOF OF LABORATORY

No.	TYPE OF CLEAR COATING USED	ONE FLOW COAT		THREE BRUSH COATS		No.	TYPE OF CLEAR COATING USED	ONE FLOW COAT		THREE BRUSH COATS	
		Failure	Condition of film	Failure	Condition of film			Failure	Condition of film	Failure	Condition of film
		Days		Days				Days		Days	
958	Phenolic resin 2540 low-cook tung oil varnish, 44 gal. length; purchased	4	50% rust	12+	Few tiny blisters, slight rust under film	977	Lacquer containing equal parts by weight nitrocellulose and glycerol phthalate plasticized resin	9	Very slight rust	10	Tiny blisters, dull
959	Modified phenolic resin 2260 low-cook tung oil varnish, 44 gal. length; purchased	4	50% rust	12+	Few tiny blisters, slight rust under film	990	Combination phenolic phthalic anhydride glycerol ester-tung oil varnish, 50 gal. length	2	50% rust lower half	10	Tiny blisters, rust under film
962	Phenolic resin 2540 low-cook tung oil varnish, 44 gal. length; made in laboratory	9	Slight rust	12+	Few tiny blisters, slight rust under film	991	Ester gum-tung oil varnish, 50 gal. length; cooked at 450° F. (232° C.)	2	60% rust	10	Tiny blisters, considerable rust under film
963	Modified phenolic resin 2260 low-cook tung oil varnish, 44 gal. length; made in laboratory	4	50% rust	12	Small blisters at top, slight rust under film	993	Same as 991 except contains 2 1/2% sulfur added as dispersion in oil previous to cooking	2	50% rust	10	Tiny blisters, very dull, much rust under film
966	25 gal. tung oil-synthetic ester No. 1 varnish, containing 0.01% sulfur; cooked at 600° F. (315° C.)	4	50% rust	12	Tiny blisters, slight rust under film	994	Commercial 4-hour varnish extended with 20% bodied tung oil	9	50% rust lower half	10	Tiny blisters, slight rust under film
967	44 gal. synthetic ester No. 1-tung oil varnish containing 0.05% sulfur; low-cook	2	70% rust	3	Large blisters, considerable rusting	995	Commercial 4-hour varnish extended with 20% bodied tung oil containing 1% sulfur	9	50% rust	10	Tiny blisters, slight rust under film
968	44 gal. ester gum-tung oil varnish containing 0.1% sulfur; low-cook	4	50% rust	5	Fairly large blisters, considerable rusting	996	50% rosin, 50% mineral spirits	1	100% rust	5	Entirely rusted
969	Lacquer made with equal parts nitrocellulose and glycerol ester PRX	9	Very slight rust	12	Tiny rust spots, dull	997	Boiled linseed oil	2	100% rust	1	Entirely rusted and disintegrated
972	Phenol resin 5000-tung oil varnish, 50 gal. length; made at laboratory; slow drying	4	50% rust	12	Tiny blisters, slight rust under film	998	Blown tung oil liquid containing 33% non-volatile matter	2	70% rust	10	Many small blisters, considerable rust
975	Viscous lead tung-ate liquid containing 32% non-volatile matter	4	100% rust	1	Badly whitened and rusted	999	50% vinyl acetate, 50% toluene	2	60% rust		Not included
976	Commercial kauri spar varnish	4	30% rust	10	Tiny blisters, considerable rust under film	1000	Synthetic ester No. 1-tung oil varnish, 50 gal. length; tung oil first treated to induce formation of β -eleostearin by irradiation and iodine treatment	9	20% rust	12	Tiny blisters, some rust under film
						1039	Modern rubber varnish (GH), baked			2	Entirely rusted and disintegrated

cm.) in size, the backs and edges of which are sealed with two or three coats of protective paint. Even under these conditions the face of the panels may sometimes show absorption of sea water to such an extent as to cause slight raising of the grain and black spots which resemble mildew.

It was interesting to observe that in the salt-water test, linseed oil (which, when exposed to the air, is of greater durability than most varnishes) failed with extreme rapidity. This was due to the fact that linseed oil films are very porous and allow salt water to go through and quickly attack the iron, causing corrosion which rapidly disrupts the film. This is a further indication that coatings for exposure under water should be formulated with resins or in other fashion to produce relatively impermeable films.

COMPARISON OF WASHINGTON AND GAINESVILLE TESTS

In considering the other tests reported in Tables I, II, and III, it would appear that normal exposure of panels to the air at Washington and at Gainesville showed the superiority of low-cook phenolic or modified phenolic resin varnishes as compared to those made with ordinary resins. It is probable that the former types are at least 100 per cent more durable than the latter. Apparently great improvement has been effected in the production of long-oil varnishes for exterior use. However, it should be pointed out that the durability of varnishes made from the newer synthetic resins may to some extent be due to the fact that they are of great oil length and are cooked at low temperatures (approximately 450° F. or 232° C.). This may possibly limit their use in some fields.

For instance, some very durable long-oil exterior varnishes may not be entirely satisfactory for floors or for permanently white non-skinning enamels. Similarly, certain glycerol-base resins have remarkable exterior durability but may have such poor initial air-drying properties as to restrict their use. It would appear, therefore, that the resin selected for a varnish must to a great extent depend upon the characteristic and physical properties which are desired.

TABLE III. TESTS OF CLEAR VARNISHES ON STEEL (2 BRUSH COATS), AIR EXPOSURE

No.	VARNISH	(Inspection after 14 weeks' exposure)	
		WASHINGTON ROOF, JULY 22, 1931	GAINESVILLE, FLA., JULY 30, 1931
958	Phenolic resin 2540 low-cook tung oil varnish, 44 gal. length; 64% non-volatile matter	Few slight rust spots under film, good gloss, good condition	Few tiny rust spots, good gloss, good condition
962	Modified phenol resin 2540 low-cook tung oil varnish, 44 gal. length; 64% non-volatile matter	Slight rust spotting under film, good gloss, good condition	A few tiny rust spots, good gloss, good condition
963	Modified phenol resin 2260 low-cook tung oil varnish, 44 gal. length; 50% non-volatile matter	Slight rust under film, fair condition	Small rust spots under film, fairly good gloss, fairly good condition
964	Ester gum-tung oil varnish, 30 gal. length; 46% non-volatile matter; 600° F. (315° C.) cook	Very pronounced rust and checking in 6 weeks; removed from test in 10 weeks; failed	Rust below film, very dull
965	Synthetic ester No. 1-tung oil varnish containing 0.1% sulfur, 25 gal. length; 58.6% non-volatile matter	Very pronounced rust and checking in 6 weeks; removed from test in 10 weeks; failed	Rust below film; checked, very dull, poor condition

Note. When tested in the high amperage arc or the Uviarc accelerated tank in the laboratory for a period of 35 days, panels 958, 960, and 962 usually indicated excellent gloss and good condition. Panel 963 developed slight rust under the Uviarc lamp. Panel 964 showed pronounced rust under both lamps.

White enamels prepared with 20 per cent Titanox, 20 per cent pure zinc sulfide, and 60 per cent of the varnishes referred to above were exposed for 14 weeks at Washington and at Gainesville. Panels 958, 960, and 962 showed strong lemon-yellow tints and tiny rust spots. Panel 963 remained very white and free from rust. All showed heavy chalking. A pale pink color is starting to develop on some of the panels, but it is not yet sufficiently prominent to determine whether it is due to rust or to some oxidation product of the resins employed.

It may also be of interest to note that in the comparative exposure of varnishes at Washington and at Gainesville during the summer months the results at Washington seem to

be slightly more rapid than at Gainesville. At Washington the panels are sprayed with water every day between twelve and one o'clock.

Exposures of lacquer coatings during the last two years have indicated the value of two types of glycerol-base resins. These two types of resins have proved superior to others employed in the formulation of lacquer that is to be exposed out of doors. They have also stood up very well in the salt water-air exposures.

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Measurement of Slow Gas Flow

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MEASUREMENT of very slow gas flow often presents serious difficulty, for standard metering equipment is inaccurate outside rather closely defined limits. Since such problems may arise to plague other investigators from time to time, it has been thought worth while to present here for their benefit a method employed by the writer. It is neither new in principle nor in detail, but rather belongs among those things whose simplicity has allowed them to be generally forgotten. A method quite similar in principle is applied to measurements in the manufactured-gas industry.

The particular problem had to do with variations in flow of carbon dioxide by convection in a closed flue system. Because of the limitations of anemometers and the problem in hand, it was impractical to use them. The velocities to be measured were too small to give satisfactory readings with a Pitot tube, and the use of an orifice (which also would have given a reading too small for accuracy) would have restricted flow to an unpermissible extent.

It was finally decided to use the thermal characteristics of the gas as a means of measurement. Two methods suggested themselves for this purpose: (1) measurement of the change of temperature of a radiator supplied with constant heat with changes of gas velocity; and (2) measurement of the change of temperature of the gas when supplied with a measured heat input.

The first method offered several difficulties not readily overcome, largely involved in the radiation characteristics of the radiator itself and the difficulty of standardization. The second, although involving possible sources of error, seemed to be simpler to utilize. The results were probably accurate to 10 per cent as used, and under the other conditions of the experiment this seemed fairly satisfactory.

The equipment required was extremely simple and easy to install. It consisted of a heating coil, a voltmeter, an ammeter, and two thermometers carefully compared for accuracy.

The heating coil consisted of a length of ordinary resistance wire wound on a non-conducting form. This was suspended in the gas stream in such a way as to give maximum contact between the wire and the gas. The form is merely an open frame designed to reduce flow resistance and is sufficiently smaller than the duct in which it is suspended to prevent high radiation loss to the duct. The duct itself is best lined for a short distance on either side of the radiator with sheet asbestos or other non-conducting material to avoid the error introduced by conduction of the duct wall.

The two thermometers are placed with their bulbs as nearly as possible in the center of the duct, at some distance on each side of the radiator, with shields so placed as to reduce errors in their readings caused by radiation. There were about five diameters between each thermometer and the radiator, which proved satisfactory. It is, of course, essential to be able to read very accurately the difference in temperature between the two thermometers, as this is a limiting factor in the accuracy of the method. Mercury thermometers that can be read to a tenth of a degree serve quite well.

In operation, a measured amount of current is passed through the resistance unit which is kept at a relatively low temperature, and the difference in temperature of the gas before and after passing it is carefully measured.

It is, of course, necessary to know the specific heat of the gas for this method to be applicable, but having that, it yields fairly close results.

The calculation of rate of flow from the observed data is easily made by the following formula:

$$F = \frac{(V \times A \times K)}{(\text{Sp. H.} \times (T - T_o))}$$

where F = rate of flow

V = impressed voltage

A = amperage

Sp. H. = specific heat of gas

T_o = temperature of gas before passing heater

T = temperature of gas after passing heater

K = constant for converting wattage to calories or B. t. u. per unit of time

If temperature is expressed in centigrade, $K = 0.860$, and gives F in kilograms per hour. If temperature is expressed in Fahrenheit, $K = 3.412$, and gives F in pounds per hour.

There are several fairly obvious errors in this method of measurement, but if care is taken in the installation of the resistance and thermometers, and if readings are carefully made, low velocities can be determined with greater accuracy than by any other simple method.

The installation of such a device in pipes carrying gases is relatively simple. The precautions to be especially observed are as follows:

1. Carefully isolate heater from the pipe walls to reduce heat losses by a conduction and radiation. A small loss by convection cannot be avoided.

2. In applying heat to the radiator, care must be exercised to prevent its becoming red hot, and its temperature should be kept as low as possible. It is preferable to use a long resistance wire which can be heated to a low temperature rather than a

short condensed heating surface at a higher temperature. The loss of heat by radiation to the pipe may be serious, but the effect of radiation on the two thermometers is identical and hence causes no error.

3. The temperature difference produced in the gas must be great enough to be read accurately on the thermometers used, but should be kept as low as is compatible with accuracy to prevent excessive heat losses to the surroundings.

4. Thermometers should be placed at a sufficient distance from the heating element to allow the gas temperature to equalize throughout the stream, but not far enough to allow a substantial amount of heat to escape from the gas to the pipe. In the experiments of this laboratory the pipe was 5 inches (12.7 cm.) in diameter and the thermometers were placed 25 inches (63.5 cm.) on each side of the heater.

5. A sheet asbestos lining placed in the pipe from thermometer to thermometer increases the accuracy of measurement.

It was possible to measure, with a simple adaptation of this method, gas velocities through a 5-inch pipe of 40 to 100 pounds of carbon dioxide gas per hour (1 linear foot per second and higher) at a pressure head too small to measure without materially interfering with gas flow. It is, of course, possible to apply this method to liquid-flow measurements, but in general it is more easily adapted to gas-flow measurements because of the large amount of heat required to change the temperature of liquids.

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Iodometric Determination of Carbon Disulfide

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METHODS of determining carbon disulfide may be classified roughly in two main divisions, the one involving oxidation to and determination as sulfate, and the other involving conversion to and determination as xanthate. When small quantities of carbon disulfide are being measured, the gravimetric determination of sulfate becomes difficult. Volumetric methods, such as metathesis with barium chromate and iodometric titration of the chromate (24) and the alkalimetric titration of benzidine sulfate (23), require more technic and time than is ordinarily desirable. This may be said to be true also of the xanthate methods which involve precipitation with a copper salt (3, 8, 10, 12-17, 19-22, 25). The situation is further complicated by the fact that xanthates, especially the free acid, are quite unstable (18); thus a method that is very rapid is to be desired.

After a thorough search of the literature and considerable research work in the laboratory on the different methods which might be used for determining small amounts of carbon disulfide, the iodometric titration of xanthate was found to be the most accurate and convenient. Therefore, it will be described in detail.

PREVIOUS EXPERIMENTS

Although it has been called a new method for the determination of carbon disulfide by Cundall et al. in 1929 (4), the iodometric titration of xanthate solutions is fairly old.

Zeise (26), in 1835, ascertained that when cupric salts are added to xanthate the copper is reduced, forming the yellow precipitate of cuprous xanthate, and that a portion of the xanthate is used up to form an oily product. In studying this product in 1845, Zeise (27) thought that it might be more easily produced by the action of iodine on xanthate. This is true; but in his experimentation Zeise was misled by the white suspension of the resultant dixanthogen, identical in appearance with the suspension of sulfur obtained when a sulfide is titrated with iodine, to believe that sulfur was precipitated. The oil that remained in solution gave, on distillation, diethyl dithiocarbonate and, assuming that this

THE DETERMINATION of carbon disulfide by iodometric titration of xanthate is of quantitative accuracy and has the important advantage of being very easily and quickly carried out. In this respect it stands in marked contrast to other methods, as the operations of precipitating, letting stand for several hours to insure complete precipitation, and filtering are completely eliminated. Essential precautions are that the alcoholic alkali used to absorb or to react with the carbon disulfide be fresh, that the formation of any appreciable proportion of free xanthic acid be avoided, and that the titration be made as soon as is feasible after forming the xanthate.

was the principal product, Zeise declared the action of iodine on xanthate to be essentially different from that of cupric salts. Later in 1847 he (28) and also Cahours (2), in 1846, obtained dimethyl dithiocarbonate by a similar procedure, using methyl alcohol in place of ethyl alcohol for preparing the xanthate.

This confusion was cleared up by Desains (7) in 1847, who showed that the principal product of the action of iodine on xanthate is, in fact, dixanthogen, $(C_2H_5OCS)_2S_2$; that no sulfur is deposited; and that the

methyl xanthate gives the strictly analogous methyl compound.

In 1849 Debus (5) showed that the oily product formed by the action of cupric salts on xanthate and that formed by iodine have the same composition, and are either the same compound or isomers.

Use of this reaction for determination of carbon disulfide seems to have been proposed first by Delachanal and Mermet (6) in 1877, who suggested acidifying the xanthate solution with acetic acid, adding starch, and titrating with standard iodine solution.

Gastine (9), in 1884, proposed this method for determining the carbon disulfide in gases by absorbing the carbon disulfide with absolute alcoholic potash and titrating the xanthate with iodine. He recommended that the titration be made with the solution either neutral or made slightly alkaline by acidifying with acetic acid, and then adding an excess of sodium bicarbonate.

In 1902 Rupp and Krauss (20) also recommended the use of an excess of sodium bicarbonate, although their data showed that more iodine was used up in such a case than when the solution was slightly acid. They believed that sulfur was also a product, doubtless being misled by the appearance of the dixanthogen, and that there was a further but much slower action of iodine on the dixanthogen.

Von Halban and Kirsch (11) in 1913, in their study of the decomposition of xanthic acid, found that the method of Gastine gave, after a little practice, reliable results. They found the reaction to be influenced neither by dilution nor by

an excess of sodium bicarbonate, but the presence of most organic solvents was found to be disturbing.

In 1923 André (1) attacked the method on the grounds that his experimental results indicated the reaction of carbon disulfide with alcoholic potash, whereby the carbon disulfide is converted to xanthate, to be not instantaneous and complete; and that, if the reaction were given sufficient time to be complete, too much iodine was used in the subsequent titration.

These anomalous results of André probably were due to neglect of certain essential precautions. Repeated experiments have shown that the reaction of carbon disulfide with alcoholic potash is complete and instantaneous if absolute alcohol be used. The presence of water slows up the reaction; but it is not necessary to eliminate all traces of water, contrary to the statements of Gastine (9), who did not seem to realize that, even if absolutely anhydrous alcohol and alkali hydroxide are used, some water is formed as soon as the two are brought together. Alcoholic alkali made up with 95 per cent alcohol reacts with sufficient rapidity, but dilution with water should be avoided.

Other experiments have shown that the high consumption of iodine upon prolonged titration reported by Rupp and Krauss and by André probably was due to the use of alcoholic alkali solutions which were not fresh. If newly made alcoholic alkali is used, the blue end point is extremely sharp and disappears very slowly; but if old or discolored alcoholic alkali is used, the blue end point disappears much more rapidly, the speed of disappearance being directly dependent on the age of the alcoholic alkali. This disappearance is aided by the presence of excess sodium bicarbonate, which therefore may be omitted with advantage, and is retarded by cooling the solution in an ice bath prior to titration.

IODOMETRIC TITRATION OF XANTHATE

Table I gives the data obtained by dissolving weighed samples of pure carbon disulfide contained in small sealed glass bulbs which were broken under 1 cc. of fresh alcoholic potash (2 cc. for the last sample), acidifying with molar acetic acid until the solution was acid to phenolphthalein but still alkaline to litmus, adding starch indicator, and immediately titrating with 0.006862 *N* iodine. No refinements of technic beyond those commonly employed by routine analysts were used.

With iodine the action is



where *X* is the xanthate radical,—SCSOEt.

TABLE I. DETERMINATION OF CARBON DISULFIDE BY IODOMETRIC TITRATION OF XANTHATE

CS ₂ TAKEN	0.006862 <i>N</i> IODINE USED	CS ₂ FOUND
Gram	Cc.	Gram
Blank	0.05	
0.0033	6.33	0.0033
0.0054	10.31	0.0054
0.0187	36.11	0.0188
0.0201	38.82	0.0202
0.0393	75.65	0.0395
0.1159	221.4	0.1156

It will be observed that the carbon disulfide found agrees exactly with that taken, within the limits of accuracy of making the weighings. Furthermore, it will be observed that, with the strength of solution used, each milligram of carbon disulfide requires about 2 cc. of iodine solution; hence, the method is applicable to minute amounts of carbon disulfide. For less than a milligram the iodine solution may be made still more dilute. In such a case the necessity of making blank determinations, using the same quantities of alcoholic alkali, water, etc., is greater than with more concentrated solutions. Instead of titrating with an iodine solution whose

strength changes rather easily, the xanthate may be determined by adding it slowly, with stirring, to a sufficiently acid mixture of standard iodate and excess iodide (which react to liberate iodine) and titrating the excess free iodine with thio-sulfate.

It is evident that the method provides a rapid and accurate means of determining the amount of carbon disulfide contained as an impurity in many materials. Indeed, it has already been used in the analysis of gases (4, 9). The necessary reagent, alcoholic caustic alkali, has been used not only to scrub out carbon disulfide in the analysis of gases (4, 8, 9, 13, 14, 15, 21), but also to extract it from liquids like benzene and motor fuel (13, 16, 19, 22, 25). In all such cases, it seems probable that the formerly used methods of analyzing the resulting xanthate solutions could be replaced by the iodometric one with much saving of time and labor.

It is perhaps unnecessary to point out that materials which themselves react with iodine would cause serious errors in the results obtained by the iodometric method. Fortunately, the most common disturbing substance, hydrogen sulfide, can be removed by previous treatment with dilute aqueous alkali. Although minute amounts of carbon disulfide may be removed also, such treatment is considered as satisfactory by workers who have published schemes for analyzing gases containing both hydrogen sulfide and carbon disulfide (4, 8, 14, 15, 21). Precipitation with ammoniacal zinc chloride has been used to remove sulfide from the xanthate solution itself (12). Other possibly interfering substances are doubtless more difficult to eliminate, as, for example, mercaptans and unsaturated hydrocarbons. Removal of dissolved gases by warming the xanthate solution, as has been done by others (13, 15), should be avoided because of the well-known instability of xanthates. Attaining the same end by means of suction, or by bubbling an inert gas through the xanthate solution, is to be preferred. In many cases, treatment with concentrated sulfuric acid before extracting the carbon disulfide may remove unsaturated compounds satisfactorily. However, it is improbable that small amounts of unsaturated hydrocarbons would react with iodine sufficiently rapidly to affect the iodometric titration of the xanthate seriously.

ACKNOWLEDGMENT

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A Precision Sodium Cutter

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THE preparation of small pellets of metallic sodium is usually effected by cutting off fragments from large commercial pieces by means of a Gattermann-style sodium knife (1). This crude method serves for most purposes, but is not well adapted to the preparation of small portions reproducibly uniform in weight.

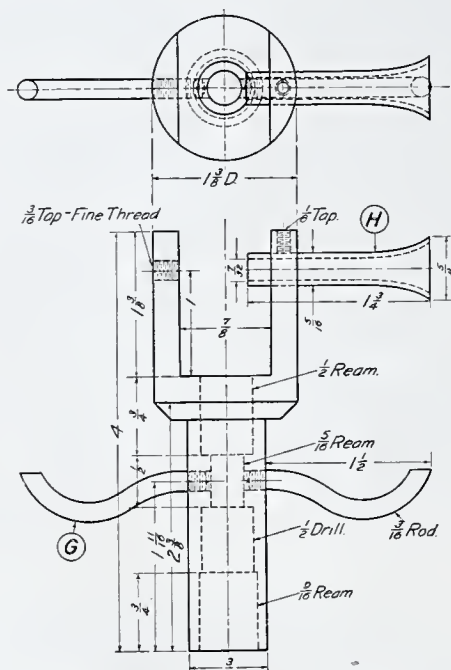


FIGURE 1. DETAILS OF BARREL

Mulliken and Gabriel (2) have suggested that a slab of sodium of given thickness be prepared, and pellets cut from this by means of a cork borer. Because of the plasticity and great reactivity of the metal, however, it is not easy to prepare slabs of precisely the right thickness. Furthermore, the resultant pellets are difficult to remove smoothly from the borer. In any case, approximately half the slab remains as a perforated plate which must be discarded or worked into wire.

In the course of research in progress in this laboratory, it became necessary to obtain uniform pieces of sodium 0.2 ± 0.003 gram in weight. Pellets of sodium of this size are used in organic qualitative analysis in the process of decomposing the organic compound prior to the tests for the elements. Since with large classes of students it is desirable to reduce the handling of sodium to a minimum, a precision cutter has been constructed and successfully employed.

This cutter consists essentially of a razor blade arranged so as to be operated by hand pressure in such a manner that uniform lengths of metal are cut from a 6- to 8-inch (15.2- to 20.3-cm.) cylindrical rod of sodium. These rods are formed by the usual sodium press (3), using a die with an

opening 5 mm. in diameter. To ensure uniform cross section, the approaches to the hole should be well rounded and the opening itself reamed and polished to a mirror surface. The 6- to 8-inch rods may be kept in a stock bottle under dry kerosene and the pellets cut off with the new cutter as may be desired.

The details of construction are indicated in the accompanying diagrams. Because of the severe alkaline conditions to which the cutter must necessarily be exposed, acidic alloys such as brass and bronze should not be used. Mild steel has proved entirely satisfactory, and stainless steel or nickel may advantageously be employed.

The method of using the cutter is as follows: Holding the cutter in such a manner that the feed tube *H* (Figure 3, vertical and the cap *D* is pressed against the palm of the hand, a length of sodium rod is inserted in tube *H* and allowed to fall until it comes in contact with the adjustable stop, *M*. The plunger is then pressed forward, the razor, *P*, cutting the sodium, and the snap button, *E*, aiding in the ejection of the pellet. Pressure on the cap is released, the plunger is returned to its normal position by the spring *I*, and the feed rod of sodium is allowed to fall by gravity or by a slight pressure of the hand until it again strikes the plate *M*, placing it in position for the cutting of the next pellet. By adjusting the

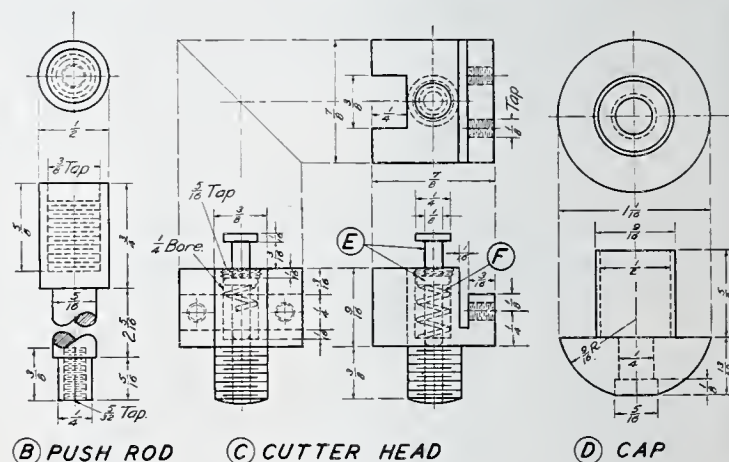


FIGURE 2. DETAILS OF PLUNGER

stop *M*, various lengths of sodium may be obtained. If desired, the feed tube *H* may have a different internal diameter from that specified in Figure 1. By these two adjustments considerable dimensional variation may be acquired.

The list of parts shown in Figures 1, 2, and 3, is as follows:

- A*, Barrel—mild steel, stainless steel, or nickel.
B, Push rod—mild steel; turn 0.002 inch smaller.
C, Cutter head—same metal as *A*.
D, Cap—same metal as *A*.
E, Snap button and spring collar— $\frac{13}{16}$ inch long; collar soldered on rod after bearing *O* has been slipped on; steel.

F, Snap button spring— $\frac{3}{16}$ inch in diameter, 1 inch long; fine steel compression spring.

G, Finger rests—make two; bent from $\frac{3}{16}$ -inch iron rod; ends screwed into barrel.

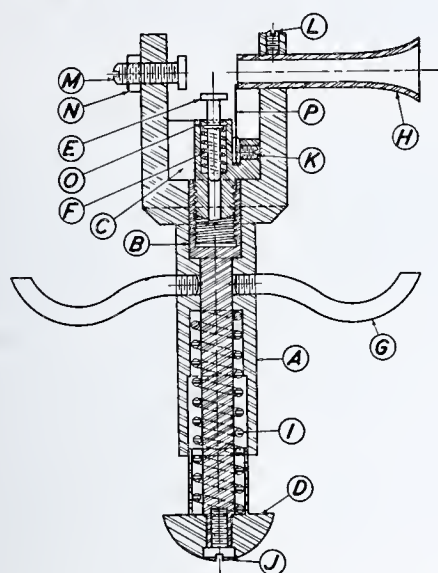


FIGURE 3. ASSEMBLY OF SODIUM CUTTER

H, Sodium feed tube—preferably of stainless steel or of nickel.

I, Plunger return spring—steel compression spring, $\frac{7}{16}$ inch in diameter, $2\frac{3}{8}$ inches long; wire 0.047 inch in diameter.

J, Cap screw— $\frac{1}{4}$ inch in diameter, $\frac{1}{2}$ inch long; fillister head.

K, Set screws—make two, $\frac{1}{8}$ inch in diameter; flat point.

L, Set screw— $\frac{1}{8}$ inch in diameter; flat point.

M, Stop— $\frac{3}{16}$ inch in diameter, $\frac{3}{4}$ inch long; make fine thread for close adjustment.

N, Lock nut—threaded for stop screw *M*.

O, Snap button upper bearing— $\frac{5}{16}$ inch in diameter; cut groove in upper face to aid in screwing in.

P, Cutter blade—safety-razor blade of Gem or Eveready type;

back of razor ground to fit groove in cutter head; blade snapped off or ground to proper length ($\frac{7}{8}$ inch) after back has been sawed through.

The reproducibility of the weights of the sodium pellets obtained is even better than that originally required. For example, with the stop set to cut a 200-mg. pellet, twelve successive units were cut from a freshly pressed rod of sodium 5 mm. in diameter. These were allowed to fall into dry benzene, later individually removed, dried quickly, and weighed on an analytical balance sensitive to 0.1 mg. Of the twelve pellets, eight weighed exactly 200 mg., two weighed 199 mg., one 201 mg., and one 202 mg. When used as described, the operation is so rapid that the amount of oxidation is negligible and the purity of the resultant units is simply the purity of the original metal. Since far more oxidation obviously occurs when the sodium pellet is heated prior to the addition of the organic compound in the test for elements than takes place in its preparation, a more detailed determination of the actual sodium content was deemed unnecessary.

ACKNOWLEDGMENT

The authors wish to thank A. A. Morton, V. F. Harrington, C. L. Gallagher, and I. S. Cliff for invaluable suggestions and criticisms.

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Determination of Tetraethyl Lead in Ethyl Gasoline

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AS MENTIONED by Edgar and Calingaert (2), the various methods published in the literature for the determination of tetraethyl lead are either too tedious or are lacking in accuracy. The bromine method published by Edgar and Calingaert (2) is rapid and accurate but sometimes troublesome, especially with gasolines rich in unsaturated compounds which require the addition of a large amount of bromine. This results in the evolution of much hydrobromic acid and, sometimes the formation of gummy precipitates which are difficult to handle, and it is the writer's experience that unless special precautions are taken, low results are obtained.

To obviate these inconveniences, the method described herein has been devised and used in this laboratory for several years.

A SIMPLE and reliable gravimetric method for the determination of tetraethyl lead in gasoline and other petroleum products is described. The method has been in use for several years in this laboratory and has given complete satisfaction. It is specially adapted for intermittent work and requires only ordinary laboratory technic. Its use in the analysis of other organo-metallic compounds is discussed.

PROCEDURE

The method depends upon the fact that tetraethyl lead is completely decomposed by shaking the gasoline solution with concentrated nitric acid, forming lead nitrate. The liquid separates into two layers and the lower layer, containing the acid with most of the lead nitrate, can be drawn

off. Since lead nitrate is not very soluble in concentrated nitric acid, the acid shaking is followed by washing in water in order to remove the last traces of lead nitrate. The reaction takes place without appreciable rise in temperature, even with gasolines rich in unsaturated compounds, and can therefore be safely carried out in a separatory funnel, using the method described below.

Measure 200 cc. of the gasoline into a 500-cc. glass-stoppered separatory funnel. Add 20 cc. of concentrated nitric

acid and shake for 15 minutes. Loosen the stopper carefully and let stand 2 minutes. The acid layer readily separates at the bottom of the funnel. In the case of some highly cracked gasolines, dark-colored compounds are sometimes formed which may obscure the line of demarcation of the two layers. This can be obviated by washing the sides of the funnel with 3 or 4 cc. of distilled water from a wash bottle.

Run the acid layer into a 200-cc. plain Pyrex beaker and set aside. Add 20 cc. of water to the funnel and shake 15 minutes. Let stand 2 minutes and draw off the lower water layer into the beaker containing the acid solution. Repeat the acid and water shaking described above, collecting the acid and water layers in the original beaker. Any emulsion which may be formed between layers and which may contain some lead is drawn off with the aqueous portion, as the small amount of organic matter which is carried along will be destroyed in the subsequent procedure.

The collected acid and water portions, which should amount to about 80 cc., are rapidly evaporated on a hot plate to a volume of 20 cc. Cool and add carefully 15 cc. of concentrated sulfuric acid; cover the beaker with a watch glass tilted with a glass hook and boil rapidly until fumes of sulfur trioxide are observed. The presence of organic matter will color the solution black, owing to the charring action of the sulfuric acid. This organic matter will be destroyed very rapidly by adding one or two drops of concentrated nitric acid (a) to the boiling solution. The reaction is very violent, but no mechanical loss should occur if the acid is added to the side of the beaker and the latter kept well covered. Continue boiling, adding nitric acid from time to time until the organic matter is all destroyed and the solution is colorless. This operation should take about 20 minutes. Cool, add carefully 20 to 25 cc. of water, stir well, and evaporate again until fumes of sulfur trioxide (b) are given off. Dilute with cold water, making the total volume up to 150 cc. Cool in ice water (c) for 1 hour and filter through an ignited and weighed Gooch crucible. Wash several times with 2 per cent sulfuric acid and finally twice with 10 cc. of 95 per cent alcohol. Dry, ignite, and weigh as lead sulfate. The amount of tetraethyl lead per gallon is calculated as follows: grams of lead sulfate per cc. of sample times the factor 2445 equals the number of cc. of tetraethyl lead per gallon. In calculating the factor 2445, the specific gravity of tetraethyl lead is taken as 1.65.

This method has been checked against the bromine precipitation method (2) on the same sample of ethyl gasoline. The results, given in Table I, show excellent agreement.

TABLE I. ANALYSIS OF ETHYL GASOLINE

METHOD USED	TETRAETHYL LEAD CONTENT		
	Cc./gal.	Cc./gal.	Cc./gal.
A	3.10	3.10	Av. 3.10
B	3.09	3.10	Av. 3.10
C	3.13	3.14	Av. 3.14

A, nitric acid extraction method; lead weighed as lead sulfate.

B, bromine precipitation method; lead weighed as lead chromate.

C, bromine precipitation method; lead determined volumetrically with ammonium molybdate.

The accuracy of the method is within 0.02 cc. of tetraethyl lead per gallon; the results obtained by this laboratory have always agreed with those of the Ethyl Gasoline Corporation's laboratories using the bromine volumetric method.

NOTES. (a) Birch (1) uses potassium nitrate for the oxidation of the organic matter. This was tried, but low results were obtained, probably owing to increased solubility of lead sulfate in the presence of potassium sulfate. Oxidation of the organic matter proceeds much faster with nitric acid than with potassium nitrate.

(b) The second evaporation is generally necessary, since concentrated sulfuric acid sometimes holds nitric oxides rather tenaciously. The presence of these oxides tends to give low results by increasing the solubility of lead sulfate.

(c) Cooling 1 hour in ice water or letting stand overnight gave the same results. Slightly lower results were obtained on filtering after standing 3 hours at room temperature.

TIME REQUIRED

The time required for a tetraethyl lead determination by the nitric acid extraction method is about 4 hours. The shaking operation described in the first part of the method can be done by hand when only one sample is being analyzed. For routine work, many determinations can be made simultaneously by using a suitable shaking machine capable of accommodating a number of separatory funnels.

The time required for complete decomposition and extraction has been determined by the following experiment:

A solution of tetraethyl lead in gasoline was made up to contain about 3.0 cc. of tetraethyl lead per gallon. Several samples of this solution were analyzed as described in the method, except that the shaking was carried on for various lengths of time. The results are given in Table II.

TABLE II. TIME NECESSARY FOR COMPLETE EXTRACTION OF $\text{Pb}(\text{C}_2\text{H}_5)_4$ FROM GASOLINE

TIME OF SHAKING	$\text{Pb}(\text{C}_2\text{H}_5)_4$ EXTRACTED
Min.	Cc./gal.
3	2.09
6	3.16
9	3.20
12	3.27
15	3.27

Another experiment showed that a single nitric acid treatment for 30 minutes followed by a water shaking for the same length of time removed only 98 per cent of the tetraethyl lead.

The results of the above experiments indicate that the minimum shaking time is 12 minutes and that the operation must be repeated for the complete extraction of the lead.

FURTHER APPLICATIONS

Many other organo-metallic compounds soluble in gasoline can be decomposed and the metal extracted with nitric acid by the method just described. This has been used, for instance, in the determination of bismuth, iron, and zinc compounds as well as for the decomposition of many metallic soaps present in compounded oils. When the metallic compounds are dissolved in a heavier petroleum fraction, such as gas oil or lubricating oils, the sample is diluted with a gasoline free from unsaturates and the extraction carried out as described.

The process outlined for destroying the organic matter is useful in the analysis of organic compounds containing such elements as lead, mercury, or antimony, which are too volatile to be estimated by ashing the sample. If the material is not soluble in gasoline, the sample can be treated directly with nitric acid, fumed with sulfuric acid, and the organic matter destroyed with nitric acid, as previously described. The metal is thus obtained in a sulfuric acid solution from which it can be determined by the usual analytical methods.

ACKNOWLEDGMENT

The author wishes to acknowledge the assistance of H. C. DeHoff in carrying out the experimental work.

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Quantitative Estimations of Minute Quantities of Reducible Sulfur

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A RAPID and accurate method is required by various industries for the estimation of minute quantities of reducible sulfur in materials upon which they operate. This is particularly true of the pulp and paper industry for the production of anti-tarnishing tissue for wrapping silver-ware. The rayon industry is also interested in such a method for the control of the desulfurization process in the production of finished viscose rayon.

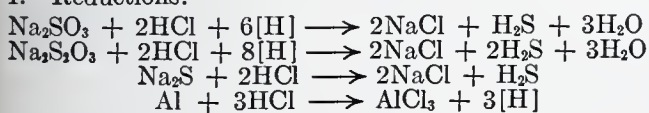
Several methods have been proposed in the past. They all depend, as does this one, upon some quantitative color reaction of hydrogen sulfide. Those of Yoe (6), Drushel and Elston (1), Sutermeister (4), Sheppard and Hudson (3), and the Technical Association of the Pulp and Paper Industry (5) are the only ones which have received any practical application by the industries. The methods of Yoe, and Sheppard and Hudson, which involve the production of methylene blue, have the drawback of requiring several days for the development of maximum color for very small quantities of sulfur. The methods of Drushel and Elston, Sutermeister, and the T. A. P. P. I., which estimate the quantity of sulfur from the stain produced on lead acetate paper by passing the evolved gases through the test paper, involve a source of considerable inaccuracy in that the stains produced tend to be spotty, owing to variations in porosity of the lead acetate paper, thus introducing difficulty in comparing them.

PRINCIPLES OF NEW METHOD

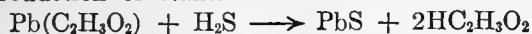
The method of the authors depends upon the slow reduction of the sulfur compounds by means of some metal which has a strong reducing action in the presence of hydrochloric acid, and subsequent sweeping of the reduced sulfur compounds, hydrogen sulfide, out of the container past a strip of dry lead acetate paper so that they meet the test strip endwise. If the evolved gases contain the hydrogen sulfide in the same concentration, stains on the test strips of comparable length and color will be obtained for successive determinations.

The reactions involved are:

I. Reductions:



II. Production of stain:



PROCEDURE

APPARATUS. Container, 250-cc. Erlenmeyer Pyrex flask, selected for symmetry of opening.

Exit tube or test-strip holder, glass tube of 6-mm. bore and

A METHOD for the determination of sulfur has been worked out which, under rigorously controlled conditions, will determine accurately from 0.000001 to 0.000015 gram of sulfur. It can be used for rough estimation of sulfur up to 0.0001 gram and may be applied to the determination of reducible sulfur in pulp and paper.

This method should be applicable to the estimation of sulfur, reducible by metallic aluminum and hydrochloric acid, in rayon, blood, urine, and other biological products, synthetic organic compounds containing sulfur, and various commercial products where the possible subsequent evolution of hydrogen sulfide may be detrimental to its use. It will not determine sulfur present as sulfates or other non-reducible forms.

any convenient length with a slight constriction 5 cm. from one end formed by softening that portion of the tube uniformly in a fine hot flame, and drawing slightly. The end of the tube nearest the constriction is rounded in the flame, but the other end is left raw, as when cut. The constricted end is inserted through a well-rolled non-porous cork stopper so that it projects through the stopper about 0.5 cm. Before each determination a fresh small wisp of Bauer and Black's best grade of absorbent cotton is placed in the extreme lower end of the tube.

A complete assembly of the apparatus is shown in Figure 1.

REAGENTS. Test strips, made by soaking sheets of Whatman's No. 40 filter paper in a solution of 1 per cent lead acetate, pressing out the excess solution (water solution) between sheets of dry filter paper,

and hanging up in the dark to dry. When dry, the sheets are pressed flat and cut into strips 5 mm. in width and of any convenient length, and stored in cork-stoppered test tubes in the dark until required for use.

Distilled water, unless otherwise specified, is made by the method of Kraus and Dexter (2) using ordinary distilled water containing a small amount of potassium permanganate and sodium hydroxide as a starting point. It is always boiled to remove any dissolved oxygen immediately before using.

Hydrochloric acid solution, made by diluting Baker's c. p. analyzed concentrated hydrochloric acid, sulfur-free, to one-third of the original volume with distilled water and kept in tightly stoppered bottles when not in use.

Sodium hydroxide solutions of various concentrations as required, with any high-grade c. p. sodium hydroxide, which has been shown by this method to be free from sulfur, made with distilled water, and containing 0.1 gram of hydroquinone per liter.

Standard solution, made by diluting a 0.5 N solution (strength determined by titration with standardized iodine solution) of sodium thiosulfate with distilled water so that it contains 0.000001 gram of sulfur per cc., and 5.0 grams of sodium hydroxide and 0.1 gram of hydroquinone per liter, and kept in the dark except when required for use.

Aluminum reductor strips, pure sheet aluminum cut into strips 1.5 by 3.0 cm. and from 1.0 to 1.5 mm. thick. They are cleaned just before using by placing them for 1 minute in boiling 1.0 per cent hydrochloric acid solution and then washing thoroughly with distilled water.

Place the weighed sample or aliquot portion of a solution of the sample in 30 cc. of 0.5 per cent sodium hydroxide solution and heat just below the boiling point for 10 minutes. Cool to room temperature, add two reductor strips and 30 cc. of the hydrochloric acid solution, and stopper immediately with the cork containing the exit tube, which has been previously steamed and dried and has had a test strip inserted so that the lower end rests on the constricted portion of the tube. At the end of 2 hours, or when the reaction has ceased, unstopper the flask and shake out the test strip, and compare with standards for from 0.000001 to 0.00001 gram of sulfur, prepared by substituting from 1 to 10 cc. of the standard sulfur solution for an equal volume of the 0.5 per cent sodium hydroxide solution in the above method. If the strips are to be kept for any length of time for reference, they should be protected from the light and atmosphere.

Fresh standard strips should be made up when the last set is not more than 2 weeks old.

In order to obtain comparable results, the above method must be adhered to strictly, as any variation from the above factors of quantity of reductor, acid concentration, and temperature gives rise to stains of indefinite color, length, and general appearance. This is shown by the following experimental observations, using 0.000010 gram of sulfur in each case.

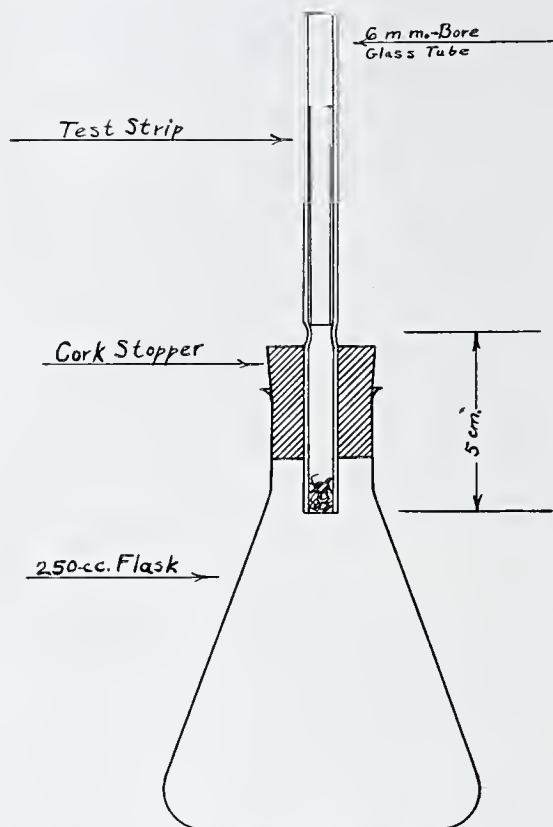


FIGURE 1. COMPLETE ASSEMBLY OF APPARATUS

QUANTITY OF REDUCTOR. 1. Placed one reductor strip in the flask in place of two. Stain equivalent to 0.000007 gram of sulfur and rather pale in color.

2. Used two reductor strips. Stain dark, with sharp boundaries and of the same length on both sides of the strip.

3. Used three reductor strips. Stains of good color and sharp boundaries, but in all of ten different trials they varied in length of stain from the equivalent of 0.000008 to 0.000009 gram of sulfur on one side of the strip, to 0.000001 or 0.000012 gram of sulfur on the other.

4. When more than three reductor strips were used, the stain ran out into a light streamer of varying length and color for two sides of any one strip.

ACID CONCENTRATION. Caused uniformly low results for amounts less than 25 cc. and uneven stains for more than 35 cc. of the acid called for.

TEMPERATURE. A matter which will ordinarily be taken care of by the heat of solution of the aluminum but, if for any reason the temperature becomes so high that drops of water form in the tube at or above the constriction, lead chloride will be formed on the stain already present, making it impossible to obtain an accurate reading. When the cotton filter is left out, the above result is always obtained.

EXPERIMENTAL RESULTS

USE OF OTHER STANDARDS. Solutions of sodium sulfide, sodium sulfite, and sodium bisulfite made up to contain 0.000001 gram of sulfur per cc. gave equivalent results to that of the chosen standard, but it was found that the sodium thiosulfate standard was much superior to the others from the point of view of keeping quality, all the others tending to fall off in strength with time.

USE OF OTHER METALS FOR REDUCTORS. With zinc, none free from sulfur is readily obtainable. Several different brands of C. P. reagent-grade zinc marked "sulfur-free" were tried

as reductors, using 1 gram of the metal per determination, and were found to contain 0.000008 to over 0.000035 gram of sulfur per gram of metal. Samples taken from the same package showed variations of up to 0.000003 gram of sulfur per gram of metal.

Magnesium and calcium were tried as substitutes for aluminum and found to be easily obtained in a form free of sulfur, but they offer the difficulty of being so highly reactive that even in small quantities in the presence of known quantities of sulfur the hydrogen is evolved so rapidly that long stains of varying color and intensity for the same amount of standard are obtained.

INFLUENCE OF HEAVY METALS IN SAMPLE. Solutions of the chlorides of copper, nickel, and lead within the same range of dilution as the standard solution were placed in measured amounts in the presence of more than enough sulfur to form cupric, nickelic, or plumbic sulfide, as the case may be, and within the limits of error of observation were found in every case to retain exactly the chemically equivalent amount of sulfur required to form the sulfides mentioned above.

RANGE OF APPLICATION. From 0.000001 to 0.000015 gram of sulfur comparable stains are obtained. Above this maximum, the amount of sulfur cannot at best be estimated any closer than multiples of 0.000005 gram of sulfur, because of variations in color and intensity of the stain on each side of the same strip. Above 0.0001 gram of sulfur the results are worthless.

USE OF ORDINARY DISTILLED WATER. The distilled water produced in the laboratory by a Barnstead still was found to contain 0.000002 gram of sulfur per 50 cc. according to this method.

EXPERIMENTAL PRACTICAL APPLICATIONS

The standard method was applied to several different commercial pulps and papers and anti-tarnish tissues, with the following results:

SAMPLE	SULFUR %
A	0.0004
B	0.0008
C	0.0012
D	0.0004
E	0.004
F	0.0008
G	0.0002
H	0.0008
I	0.0001

A, High-grade sulfite pulp, well bleached and having a mill treatment with hot 3 per cent caustic solution.

B, Unbleached sulfite pulp.

C, Same pulp as B, but having had a great deal of mechanical handling while wet.

D, Very soft and absorbent sulfite pulp that has received a very thorough bleaching and treatment with strong caustic (strength unknown) in the mill.

E, Unbleached kraft wrapping paper.

F, Same pulp as was used for E after a thorough bleaching with soda bleach.

G, H, and I, Tissues sold by three different manufacturers specifically for wrapping silver-ware.

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RECEIVED June 29, 1931. From a thesis submitted by W. W. Sweet in partial fulfillment of the requirements for the degree of bachelor of science.

Myers' Demulsification Test for Bituminous Emulsions

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WITHIN the past year a new method for determining the stability of bituminous emulsions has been suggested by Joseph E. Myers, chief chemist of the New York State Highway Department. This test has been found to be of considerable value in classifying and studying such emulsions. The method of conducting the test is here given (2, 3).

One hundred grams of emulsified asphalt are placed in a tared 600-cc. glass beaker and 35 cc. of 0.02 *N* calcium chloride solution are added during a period of approximately 2 minutes, being stirred with a glass rod. The contents of the beaker are then drained through a No. 14 sieve, and the unbroken emulsified asphalt in the beaker and on the rod is rinsed through the sieve with distilled water until there is no appreciable discoloration of the rinsing water. The beaker, rod, and sieve are then dried in an oven at 163° C. (325° F.) for 2 hours and weighed. The percentage of asphalt residue deposited in the beaker and on the rod and sieve is taken to be the difference between the weight of the beaker, rod, and sieve after drying, and their tared weight determined at the beginning of the test.

This test is founded on the tendency of calcium chloride to break an oil-in-water emulsion by the formation of an insoluble calcium soap from the alkali soap used as the emulsifier. In practice it is used to distinguish between two classes of emulsions: the quick-breaking type of bituminous emulsion which shows a high value in this test, and the slow-breaking type of bituminous emulsion which shows little or no demulsification. It is assumed that this test is indicative of the rapidity with which an emulsion will break when in contact with a given type of mineral aggregate. Insufficient work has been done as yet to show this connection in all cases. At the present time caution must be exercised in interpreting the results in highway work.

This test has been modified in practice by changing the amount and strength of calcium chloride solution used. For ready reference these various modifications are designated as follows:

- 35-02, 35 cc. of 0.02 *N* CaCl₂
- 50-01, 50 cc. of 0.01 *N* CaCl₂
- 50-02, 50 cc. of 0.02 *N* CaCl₂
- 50-10, 50 cc. of 0.10 *N* CaCl₂
- 70-01, 70 cc. of 0.01 *N* CaCl₂

These various modifications used by different laboratories have been devised to cover adequately the entire range of bituminous emulsions. It is perhaps unnecessary to retain all of these modifications. At the present time bituminous emulsions are made which show values of from 0 to 100 per cent demulsification by the original test. The range of usefulness of the test has been increased by altering the amount and concentration of the calcium chloride solution.

PRECAUTIONS

In determining the per cent demulsification of a bituminous emulsion, it has been found that in order to obtain reproducible results it is necessary to observe certain precautions not mentioned in the original method.

THE METHOD for performing the demulsification test for bituminous emulsions is discussed. It is pointed out that the standard calcium chloride should be made up precisely and that the temperature of the emulsion and the calcium chloride solution should be controlled during the test. A temperature of 25° ± 1° C. is recommended, and a sieve made of wire that will not be attacked by alkali must be used.

It is at once obvious that the strength of the calcium chloride solution must be precisely controlled. The best method of preparing a standard calcium chloride solution is that used by the American Public Health Association.

Prepare the 0.02 *N* standard calcium chloride solution by dissolving 1.0008 grams of dry calcium carbonate or pure calcite

in the least possible excess of dilute hydrochloric acid, taking care to avoid loss by spattering. Remove the excess of acid by several evaporations to dryness and make up to 1 liter.

In most cases the per cent demulsification is a function of the temperature. With certain emulsions the effect of temperature is negligible, whereas with others it is very marked. This is brought out by reference to Table I. In making these tests, both the emulsion and the calcium chloride solution were brought to the indicated temperature which was maintained during the mixing of the two. It is apparent that the temperature must be controlled with considerable accuracy, and it is recommended that 25° ± 1° C. be used.

TABLE I. RESULTS OF DEMULSIFICATION TESTS

EMULSION	At 20° C.	At 25° C.	At 30° C.
	%	%	%
	TEST 50-01		
1	1.4	1.4	2.8
2	2.8	5.7	5.7
3	1.1	1.1	1.1
4	18.3	31.0	40.9
	TEST 35-02		
	At 15° C.	At 25° C.	At 35° C.
5	1.5	7.4	14.8
6	Trace	1.5	13.2

That the test involves factors other than the formation of calcium soap is suggested by the rather pronounced temperature effect. If the reactions taking place were simple, it might be expected that some connection could be shown between the demulsification value and the quantity of calcium chloride used. For example, it might be expected that 35 cc. of 0.02 *N* calcium chloride would give the same result that would be obtained with 70 cc. of 0.01 *N* calcium chloride. That this is not the case is brought out in Table II. Further study of the mechanism involved must be made before any definite conclusions can be reached. It seems probable that dilution has some effect on the demulsification observed. It should be understood that all of the emulsions considered herein show perfect miscibility in water (1).

TABLE II. EFFECT OF DILUTION ON DEMULSIFICATION

EMULSION	(All determinations at 25° C.)			
	TEST 35-02	TEST 70-01	TEST 50-01	TEST 50-10
	%	%	%	%
1	2.8	1.4	1.4	...
2	14.3	7.2	5.7	...
3	1.1	1.1	1.1	...
4	32.7	47.5	31.0	...
5	0.0	0.0	0.0	62.7
6	0.0	0.0	0.0	100.0

Many bituminous emulsions, especially those made with a strongly alkaline emulsifier, will attack brass, solder, etc. This can be easily demonstrated by pouring a strongly alkaline

bituminous emulsion through a brass sieve on which an appreciable amount of separated asphalt will be collected. The same emulsion when poured through an iron screen of the same mesh will show no separation of asphalt. A satisfactory screen can be made by bending a piece of iron wire cloth (12 mesh; 0.028-inch diameter wire; 0.055-inch opening; this corresponds to a No. 14 standard test sieve) over the end of a cylindrical or spherical block forming a basket. A convenient size is about 3 or 4 inches (7.6 or 10.1 cm.) in diameter and 1 to 2 inches (2.5 or 5.0 cm.) deep. A piece of heavy iron wire can be caught through the upper edge to serve as a handle. No solder should be used.

Repeated tests have failed to show any difference in the results when the emulsion and calcium chloride are allowed to

stand for a considerable length of time or the asphalt is drained at once through the screen. Emulsions which show high percentages of demulsification frequently separate the asphalt in the form of a large lump which is quite likely to entrain unbroken emulsion. The calcium chloride should be added slowly with vigorous stirring in order to keep excessively large lumps of separated asphalt from forming.

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RECEIVED July 31, 1931.

A New Jelly-Strength Tester

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MEASUREMENT of jelly strength is of importance not only in the study of pectin but also in the manufacture of fruit and artificial jellies. The standardization of jellies and similar products with respect to consistency and jelly strength is much to be desired.

Paine (7) in 1922 called attention to the need of a satisfactory method of measuring the jelly strength. Since that time several jelly-strength testers have been described by Sucharipa (9), Baker (1), and Tarr (10). Fellers and Griffiths (4) have shown that the Bloom gelometer (3), originally adapted for testing gelatin (8), could be used to measure the jelly strength of fruit jellies and similar products. But these instruments are either expensive, non-mobile, or of complex construction. Their use is limited almost entirely to the laboratory.

grams is stamped on the metal cylinder and the pressure necessary to break the jelly layer may be read directly.

To eliminate the effect of the weight of the instrument tests must be made with the tester held horizontally, as shown in Figure 2. The plunger is placed on the surface or layer of the jelly to be tested and pressure is slowly applied until the surface is broken, when the plunger springs back to its original position. The leather washer marks the maximum pressure reached, which is read directly in grams from the scale.

Because of the ease of making the pressure tests, fully eight or ten measurements may be made in a minute.

Results of measurements made to test the accuracy of the instrument are shown in Table I. Apple jelly and strained cranberry sauce were prepared in quantity and poured while hot into a large number of 2-ounce straight-sided glass jars. These were paraffined to prevent surface evaporation and tested for jelly strength the following day. Several of the samples of cranberry sauce examined were from tin cans holding 21 ounces. The tests were made by cutting the jelly mass in two and determining the jelly strength of both cut surfaces. In general, the cut surface of a jelly gave more reliable pressure measurements than the outer surfaces—i. e., the top or bottom. In preparing the jellies a series was purposely included extending from soft to very firm consistency.

The probable error was calculated by use of the formula (5):

$$P. E. = 0.6745 \sqrt{\frac{\sum d_a^2}{N^2}}$$

where *P. E.* is the probable error, *d_a* the deviation from the arithmetic mean, and *N* the number of determinations.



FIGURE 1. DETAIL OF JELLY-STRENGTH TESTER

To overcome such difficulties and to supply the need for a simple tester of more general utility, the present instrument was devised. It operates on a principle similar to that utilized in several pressure testers which have been recently devised by Magness and Taylor (6), and Blake (2), for determining the maturity of pears, apples, peaches, etc.

As illustrated in Figure 1, a detachable plunger, *A*, is attached to a metal rod, *B*, which runs through a hollow metal cylinder, *C*. Bearings, *D*, for the rod are provided at either end of the cylinder. Within the hollow cylinder a spring is attached to the metal rod at one end and to the bottom bearing at the other end. This spring provides the necessary tension. An eyelet, *E*, attached to the plunger rod projects through a slot, *F*, in the cylinder and travels back and forth with the rod. On the outside of the cylinder the eyelet encircles a small rod, *G*, running parallel to the plunger rod. There is a leather washer, *H*, on this small rod which is pushed by the eyelet and marks the highest point reached by the latter. A scale registering the tension of the spring in



FIGURE 2. INSTRUMENT IN OPERATION

From Table I, the average per cent deviation from the mean in a large number of determinations is 3.51 to 4.7, indicating a reasonable accuracy for the instrument.

TABLE I. ACCURACY OF JELLY-STRENGTH MEASUREMENTS

PRODUCT	INVESTIGATOR	SAMPLE No.	MEAN JELLY STRENGTH		AV. DEVIATION FROM MEAN				PROBABLE ERROR OF MEAN		APPARENT CONSISTENCY
			Top	Bottom	Top		Bottom		Top	Bottom	
					Grams	%	Grams	%			
Apple jelly	CRF	34	85.1	68.5	3.6	4.2	4.0	5.8	0.55	0.62	Medium
	JAC	32	88.3	71.6	3.6	4.1	4.0	5.6	0.78	0.77	
Cranberry sauce A	CRF	70	122.6		3.8	3.1			0.36		Medium soft
	JAC	70	123.9		4.5	3.7			0.46		
Cranberry sauce B	CRF	60	174.1		5.8	3.4			0.61		Firm
	JAC	60	172.8		6.6	3.8			0.65		
Cranberry sauce C	CRF	10	233.1	176.4	7.7	3.3	9.7	5.5	1.74	2.88*	Very firm
	JAC	10	234.0	155.9	8.4	3.6	3.9	2.5	1.96	1.70	
Cranberry sauce D	CRF	10	251.4	161.8	6.9	2.7	9.6	5.9	2.12	2.26	Too firm, rubbery
	JAC	10	256.0	162.5	8.2	3.2	5.1	3.1	1.99	0.92	

It was found that the best method of testing jellies was to make three or more measurements on a sample. The mean of the three determinations is then taken as the jelly strength. In order to determine the accuracy of this method, samples of jelly and strained cranberry sauce were measured by different investigators and the probable error of the mean calculated in each case.

TABLE II. PROBABLE ERROR OF MEAN WHEN THREE MEASUREMENTS ARE MADE ON JELLY

SAMPLE No.	INVESTIGATOR	JELLY STRENGTHS	MEAN	PROBABLE ERROR OF MEAN
1	CRF	255, 238, 256	249.7	±3.5
1	JAC	247, 257, 250	251.3	±1.6
1	CCR	237, 260, 245	247.3	±3.7
2	CRF	84, 88, 82	84.7	±0.97
2	JAC	85, 75, 85	81.7	±1.8
3	CRF	160, 180, 170	170.0	±3.2
3	JAC	168, 179, 170	172.3	±2.8
4	CRF	129, 120, 115	121.3	±2.3
4	JAC	125, 124, 130	126.3	±1.0

Table II shows the probable error of the mean of three measurements on the same sample to vary from 0.97 to 3.7 where the jelly strengths varied from 82 to 260 grams. The

personal error was likewise slight. Because of the small probable error, the mean of three determinations on the same sample may be considered reasonably reliable. The new jelly-strength tester combines low cost, adaptability, ease and speed of operation, mobility, and simplicity. It may be purchased from John Chatillon & Sons, 85 Cliff St., New York, N. Y.

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RECEIVED August 12, 1931.

Determination of Phosphates in Waters

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THE need for a more rapid, reliable, and simplified method for the determination of phosphates in certain waters is evident. In the biological field limnologists are giving attention to the relation of phosphates to plankton content, and although primarily interested in this field, the authors have noted the recent method of Scarritt (2) for the determination of phosphates in boiler water in the presence of silicates. This method has been tried and found to have some outstanding disadvantages which can be practically entirely eliminated by the method prescribed. Scarritt's main disadvantages are that the amount of color is not sufficient; that some of the reagents are unstable; and that the color due to silicates is not obviated, the final solution not being acid. Truog and Meyer (3) have improved Denigès' method for phosphorus analysis but have not presented it in detail for water. After considerable experience with phosphorus determinations, the Denigès principle, as outlined by Kuttner and Cohen (1) and further elaborated by Youngburg and Youngburg (4), has been chosen for biological work. It is the colorimetric method whereby phosphomolybdate is reduced by stannous chloride to give an intense blue color. The concentration of the acid and the molybdate is much different from that used by Truog and Meyer, and sodium

molybdate is preferred to the ammonium salt, although either may be used. This method, here presented for waters, involves no deteriorating reagents except the dilute stannous chloride solution; the preparation of it, however, is extremely simple. The color development is immediate, the fading is slow (see Figure 1), and the amount of color obtained is greater than has been found for any other phosphorus method. The method of Truog and Meyer, however, gives only 12.5 per cent less color. The reason for this is the lower concentration of molybdate and of acid which they use. Al-

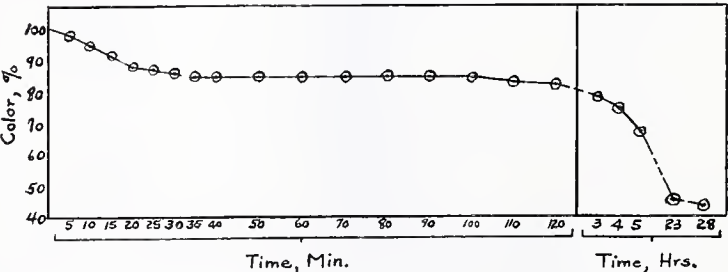


FIGURE 1. RATE OF FADING OF BLUE COLOR

though 12.5 per cent less color is not a major objection in itself, the greater the acidity of the solution the less interference of silica, and in the determination of total phosphorus,

as here indicated, the organic matter must be oxidized, and therefore the more sulfuric acid present the better. Truog and Meyer's concentration of acid is 0.4 *N*, the authors' 1.0 *N*. By reducing the concentration to that used by Truog and Meyer, the oxidation could not be done so simply.

Since the solution is strongly acid (1 *N* sulfuric acid), silica interferes practically not at all. This is shown in Table I. There can be present 3500 p. p. m. before it interferes as much as 1 p. p. m. of PO₄.

TABLE I. PRODUCTION OF BLUE COLOR BY SODIUM SILICATE

SILICATE PRESENT	COLOR DEVELOPED BY SILICATE CORRESPONDING TO PO ₄
<i>P. p. m.</i>	<i>P. p. m.</i>
100	0
200	0
600	0
800	0
900	0.05
1000	0.10
1200	0.15
1500	0.25
2000	0.35
2500	0.50
3000	0.75
4000	1.25
5000	2.00
6000	3.50

The effect of variations of temperature on the color reaction* is small. After heating the final colored solution to boiling and then cooling to 40° C., there is an increase of color of only 4 per cent. If the reagents are warmed to 50° C. before mixing, there is a loss of about 8 per cent of color. It is evident then, that nothing would be gained by heating, and that ordinary fluctuations in temperature can be disregarded.

INFLUENCE OF INTERFERING SUBSTANCES

Experiments on the influence of ferrous and ferric iron are in agreement with those of Truog and Meyer (3). Ferrous iron shows no influence up to 50 times as much iron as PO₄. Ferric iron interferes when present in more than 6 p. p. m. of iron. The interference is essentially an increase in color and the development of a greenish shade which superimposes on the blue to make reliable color comparison impossible.

Copper, added as cupric sulfate, shows little effect up to 30 to 50 times as much as PO₄. Beyond this, the solution begins to show a greenish tint which increases proportionately with the copper added.

Carbonates and sulfates do not interfere in even as much as 400 times the amount of PO₄ present, and aluminum up to 50 times the amount of PO₄ does not interfere. Nitrates may be present in considerable quantity without appreciably depressing the formation of the blue color, as shown in Table II.

TABLE II. INTERFERENCE OF NITRATES

PO ₄	N AS NaNO ₃	RECOVERY
<i>P. p. m.</i>	<i>P. p. m.</i>	%
5	15	100
5	25	98
5	50	96
5	75	96
5	100	95
5	200	93
5	300	85
5	400	83
5	500	82
5	1000	71

The interference of various other substances has been ascertained by Kuttner and Cohen, and Truog and Meyer.

ACCURACY OF METHOD

One part of PO₄ can be detected in 100 million parts of water. The quantitative recovery is shown in Table III.

For this work a Spencer Duboscq colorimeter was used and the matching of the colors was done under very good conditions.

TABLE III. RECOVERY OF PHOSPHATE FROM WATER

PO ₄ IN ORIGINAL WATER	PO ₄ ADDED	TOTAL EXPECTED	RECOVERED	LOSS	RECOVERY
<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>	%
2	0.5	2.5	2.475	0.025	99.0
2	2	4	3.94	0.060	98.5
2	5	7	6.82	0.180	97.4
2	8	10	9.84	0.160	98.4
2	18	20	19.80	0.200	99.0
2	23	25	24.50	0.500	98.0
2	28	30	29.55	0.450	98.5
2	38	40	39.04	0.960	97.6
2	48	50	49.25	0.750	98.5

SPECIAL REAGENTS REQUIRED. 1. Ten *N* sulfuric acid. Add 450 cc. of concentrated c. p. sulfuric acid to 1100 cc. of water. Titrate the solution and dilute to make 10 *N*. If not too great accuracy is required, it is sufficient to mix 450 cc. of concentrated acid with 1156 cc. of water and to omit the titration.

2. Molybdate-sulfuric acid solution. Mix 500 cc. of 7.5 per cent sodium molybdate, c. p. (phosphorus-free), with 500 cc. of 10 *N* sulfuric acid. Ammonium molybdate may be used. With the samples employed, a 12.8 per cent solution of either (NH₄)₂MoO₄ or the hepta salt, (NH₄)₆Mo₇O₂₄·4H₂O, was equivalent to 7.5 per cent of sodium molybdate, Na₂MoO₄·2H₂O.

3. Stannous chloride solutions. For the stock solution, dissolve 10 grams of stannous chloride, SnCl₂, c. p., in 25 cc. of concentrated hydrochloric acid, c. p. (warming is permissible). Store in a brown, glass-stoppered bottle.

For the dilute solution, dilute 1 cc. of the above stock solution to 200 cc. with water. This reagent is safe to use for a week or until a turbidity forms, after which a new dilution should be made.

4. Standard phosphate solution. Dissolve 2.506 grams of pure, dry, monopotassium phosphate (KH₂PO₄) in water to make 100 cc.

For natural water analysis, dilute 2 cc. of this stock solution to 1000 cc. (1 cc. when diluted to 35 cc. = 1 p. p. m. of PO₄).

For boiler water analysis, dilute 10 cc. to 1000 cc. (1 cc. when diluted to 35 cc. = 5 p. p. m. of PO₄).

PROCEDURE. The method is prescribed for a total volume of 50 cc. Place 35 cc. of the water in a large test tube (200 by 25 mm.) graduated at 35 cc. and 50 cc. For less accurate work a graduated cylinder may be used.

To two similar tubes add 1 cc. and 10 cc., respectively, of standard phosphate solution. Then make up the contents of the two tubes to the 35-cc. mark with water.

To each of the three tubes add 10 cc. of molybdate-sulfuric acid solution, then 5 cc. of the dilute stannous chloride solution, and mix the contents well at once.

Match the colors with a colorimeter or with the naked eye, depending on the accuracy desired.

Standards of intermediate concentrations may, of course, be prepared by taking amounts of phosphate solution between 1 cc. and 10 cc.

CALCULATION		
STANDARD PHOSPHATE SOLN. MATCHED BY WATER	PO ₄ IN NATURAL WATER	PO ₄ IN BOILER WATER
<i>Cc.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
1	1	5
2	2	10
3	3	15
4	4	20
5	5	25
6	6	30
7	7	35
8	8	40
9	9	45
10	10	50

Reading of standard

Reading of water

 × standard in p. p. m. =
p. p. m. of PO₄ in water

EXAMPLE. If 5 cc. of standard phosphate solution (25 p. p. m. of PO_4) were used, the reading of the standard was 20 mm., and that of the water 24 mm., then $20/24 \times 25 =$ p. p. m. of PO_4 in the water.

The procedure is the same for any of the water analyses, except that for natural waters the more dilute standard phosphate is used.

For the determination of total phosphorus in plankton water, the sample must be evaporated to near dryness and

the organic matter oxidized by digesting with sulfuric acid and perhydrol according to Youngburg and Youngburg (4).

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Potentiometric Titration of Acidity in Oils

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THE A. S. T. M. recommendation (1) for the determination of acidity of oils, though extensively used, is subject to several limitations. The use of phenolphthalein and other indicators (3) for detecting the end point of an oil titration is obviously unsatisfactory in the case of dark-colored oils because of the difficulty of observing the indicator change. Another disadvantage is the fact that most oils are not completely soluble in the hot alcohol solution. A two-phase system results, and the success of the determination of the acidity of the oil is dependent upon the distribution of the acidic ingredient between the two phases. Seltz and McKinney (6) have shown the possibility of the detection of the potentiometric end point for oil titration in isoamyl or *n*-butyl alcohol solutions. Later Seltz and Silverman (7) suggested improvements in the apparatus by substitution of a silver-silver chloride electrode for the quinhydrone reference electrode and its agar-agar bridge.

The work to be described was undertaken in connection with the research on the deterioration of high-tension cable now in progress in this laboratory. It represents an attempt to develop the potentiometric method as a practical laboratory means of determining acidity in small samples of oil obtained at different points in the cable insulation.

SOLVENTS

For use in titration work and especially in potentiometric titrations, a solvent should be capable of effectively dissolving the sample, the titrating agent, and the "conducting salt," and should possess a dielectric constant sufficiently high to permit the desired ionic reaction to take place rapidly, as well as to permit ionization of the conducting salt in order to increase the conductivity of the solution. Both isoamyl and *n*-butyl alcohol are excellent oil solvents, are satisfactory solvents for potassium hydroxide and lithium chloride (used as conducting salt), and have dielectric constants of about 15 to 18 (5).

In the work to be described the solution used as a solvent for the oil was isoamyl alcohol saturated with lithium chloride in order to give higher conductivity. The neutralizing solution consisted of a 0.025 to 0.050 *N* solution of potassium hydroxide in isoamyl alcohol standardized against Bureau of Standards benzoic acid.

THE PLATINUM-CARBON electrode couple is shown to possess distinct advantages over others previously suggested for the acidimetric titration of oils.

An explanation of the second inflection point in the differential plot of results on oil titrations is postulated as being due to the presence of two different classes of organic acids.

A system is described which permits acidity determinations on oil samples as small as 0.5 gram.

Blank determinations on the solvent were made frequently and required only 0.10 to 0.15 cc. of alkali.

APPARATUS

Several difficulties encountered in the use of the agar-agar bridge of Seltz and McKinney (6) have been experienced in preliminary work in this laboratory, chief among which was a tendency of the agar-agar to dehydrate slowly and permit leakage. Isolation of the reference electrode in a separate vessel through use of a bridge was found to be impractical because of the relatively high resistance of the solution. The silver-silver chloride electrode, when used as described by Seltz and Silverman (7), proved quite satisfactory if freshly prepared, but after some days ceased to function as a standard. Such a deterioration was shown by the failure of the electrodes to give any potential break at the end point. In both of these systems (6, 7) a quinhy-

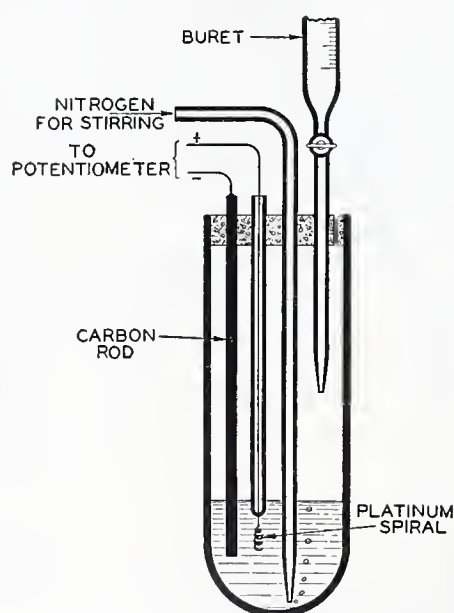


FIGURE 1. CELL FOR POTENTIOMETRIC TITRATIONS

drone electrode served as the indicator electrode. This quinhydrone electrode itself was found to be slow in coming to equilibrium potential in addition to its potential being notably unreliable in alkaline solutions.

Holt and Kahlenberg (4) have shown that certain metals and non-metals coupled together are very satisfactory end-point indicators in acidimetric titrations. Some of these recommended couples failed entirely when tried in non-aqueous solutions, but the platinum-carbon pair proved to be quite excellent. Inasmuch as carbon and natural graphite gave equally good results, small arc-light carbons were used.

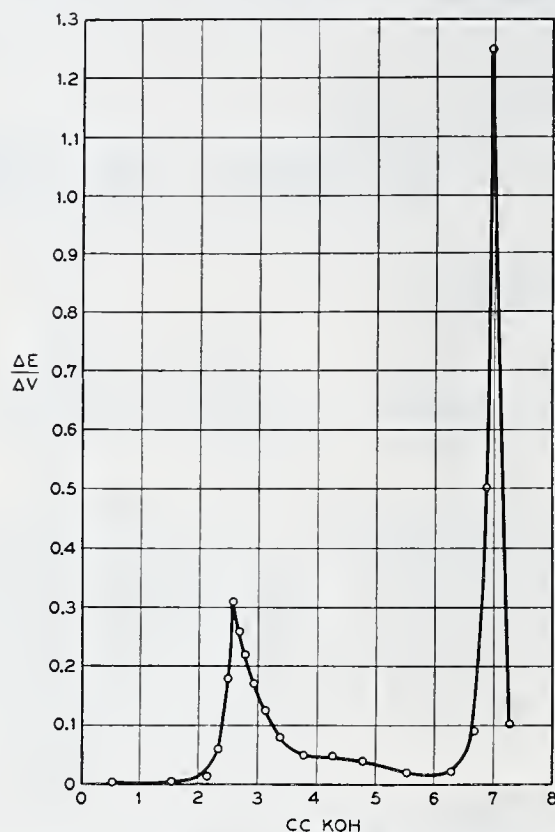


FIGURE 2. TITRATION CURVE FOR MIXTURE OF PICRIC AND BENZOIC ACIDS USING PLATINUM AND CARBON ELECTRODES

The advantages of this electrode pair are (1) simplicity, (2) compactness, (3) high electrical conductivity, (4) low resistance contact with the solution, and (5) large potential change at the end point (100 to 250 millivolts).

Figure 1 shows the apparatus that was used in titrations wherever possible,¹ including cell, electrodes, buret, and nitrogen-stirring arrangement. The buret was of 10 cc. capacity, graduated in 0.05-cc. divisions, and carried an extended tip for convenience in passing through the cell stopper. A Leeds and Northrup hydrogen-ion type potentiometer was used in conjunction with a Weston model 440 table-type galvanometer.

TABLE I. ACIDITY OF A TURBINE OIL USING A PLATINUM-CARBON COUPLE

DETERMINATION	ACID NUMBER Mg. KOH/grams oil	DEVN. FROM MEAN Mg. KOH/grams oil
1	4.74	+0.12
2	4.62	0.00
3	4.44	-0.18
4	4.76	+0.14
5	4.65	+0.03
6	4.73	+0.11
7	4.54	-0.08
8	4.48	-0.14
9	4.72	+0.10
10	4.61	-0.01
11	4.48	-0.14
12	4.61	-0.01

Mean 4.62

Max. devn. from mean, 0.18 (3.9%).

Av. devn. from mean, 0.10 (2.6%).

Table I shows some typical results of titrations of unfiltered turbine oil using the platinum-carbon electrodes. Weighed samples of from 1.00 to 2.00 grams were used.

¹ In titrations where the agar-agar bridge and differential electrode systems were used a somewhat larger cell was necessary.

The series of measurements was extended over a period of about six weeks.

In the titration of turbine oils a double inflection could be found with any electrode system that functioned at all satisfactorily in isoamyl alcohol solutions. This has suggested the possibility of the presence in the oils of acidic ingredients possessing widely different ionization constants. To check up on this point, a number of acid mixtures have been titrated using the platinum-carbon electrode pair and some of the results are represented graphically in Figures 2 and 3. Since the end points of the component acids may be detected in this manner, it should be possible to distinguish between acids having widely different ionization tendencies when present in oils. For this reason the writers believe the two inflections to be caused by the different types of acids present in oils.

ADAPTATIONS FOR SMALL SAMPLES

Previous work reported (2, 6, 7) on the potentiometric determination of acidity of oils has specified oil samples of the order of 10 to 20 grams per determination. The necessity arose for determining the acidity of oil samples of less than 1 gram. Accordingly, a cell of Pyrex (Figure 1) was designed to take the place of the 250-cc. flask previously used. This smaller cell had an inside diameter of 3 cm. and a height of 12 to 15 cm. In this cell, 25 cc. of solvent were used with an oil sample of 0.5 to 2.0 grams (or 0.020 gram of ben-

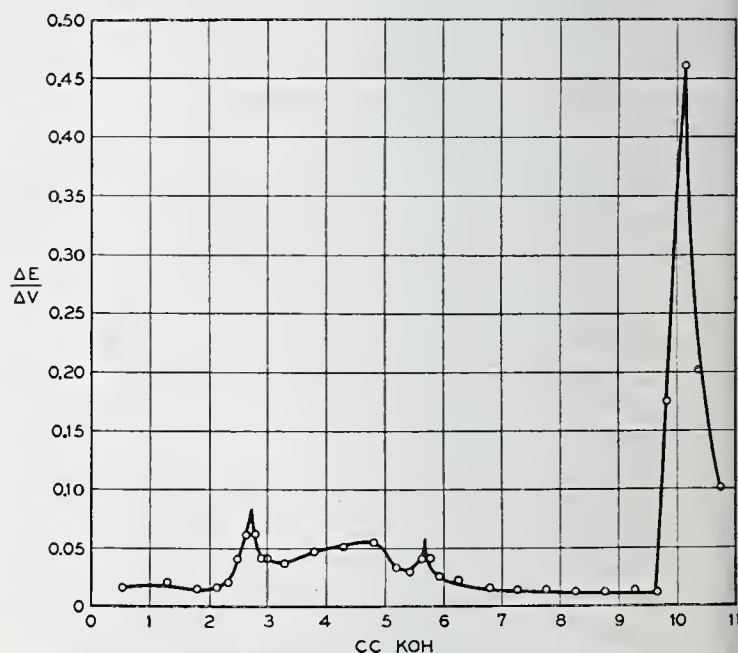


FIGURE 3. TITRATION CURVE FOR MIXTURE OF STEARIC, BENZOIC, AND PICRIC ACIDS USING PLATINUM AND CARBON ELECTRODES

zoic acid when standardizing alkali). This cell and equipment have been used quite extensively with satisfactory results.

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Ashing Plant Materials to Determine Total Phosphorus

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A METHOD has been worked out¹ which offers some advantages over the somewhat tedious and time-consuming standard magnesium nitrate method for oxidizing plant samples for total phosphorus determination. It consists essentially of mixing the weighed sample with an excess of pure calcium carbonate and igniting until the whole is perfectly white. This method is very rapid, requiring but 20 to 30 minutes for large samples. It can be used with widely varying types of plant material. There is no danger of spattering and consequent loss of material, it produces no disagreeable fumes, and the residue is rapidly and easily decomposed and brought into solution with dilute nitric acid. In the process of ignition the silica is completely dehydrated and may be filtered out, or if the amount is small, that step may be omitted as it does not disturb the accuracy of the determination which follows. As many as forty or fifty total phosphorus determinations may be carried out on plant materials in a day using this method of ashing.

TABLE I. RECOVERY OF PHOSPHORUS ADDED TO BLANKS IN CALCIUM CARBONATE METHOD

SAMPLE	BASE USED (1 cc. ≈ 0.000207 Gram P)	ACID ADDED (1 cc. ≈ 0.000204 Gram P)	P RECOVERED Gram	P ADDED Gram	DEVN. Gram
	Cc.	Cc.			
1	15.9	10.0	0.0012	0.0011	+0.0001
2	17.3	9.0	0.0017	0.0017	0.0000
3	15.3	4.1	0.0023	0.0022	+0.0001
4	20.0	6.9	0.0027	0.0028	-0.0001
5	20.3	4.3	0.0033	0.0033	-0.0000
6	25.3	7.4	0.0037	0.0039	-0.0002
7	25.0	3.0	0.0046	0.0046	0.0000

TABLE II. COMPARATIVE PHOSPHORUS CONTENT OF DRIED GROUND CORN BLADES BY TWO METHODS

SAMPLE	MAGNESIUM NITRATE METHOD KOH (1 cc. ≈ 0.000207 Gram P)			CALCIUM CARBONATE METHOD KOH (1 cc. ≈ 0.000207 Gram P)		
	Cc.	Gram	%	Cc.	Gram	%
1	17.4	0.0036	0.36	16.9	0.0035	0.35
2	16.9	0.0035	0.35	16.9	0.0035	0.35
3	16.0	0.0033	0.33	16.4	0.0034	0.34
4	17.4	0.0036	0.36	16.9	0.0035	0.35
5	16.0	0.0033	0.33	16.9	0.0035	0.35
6	17.4	0.0036	0.36	16.9	0.0035	0.35
7	16.9	0.0035	0.35	16.9	0.0035	0.35
8	16.4	0.0034	0.34	16.4	0.0034	0.34
Av.			0.347	Av.		
Std. devn.			0.012	Std. devn.		

PROCEDURE

Weigh a 1-gram sample into a nickel or iron crucible and mix thoroughly with 2 grams of pure precipitated calcium carbonate. Shake the mixture firmly into the bottom of the crucible, then cover completely with a thin layer of calcium carbonate (1 or 2 grams usually suffice), and heat the crucible gently on a triangle with a Meker burner until fumes are no longer evolved. Ignite at the full heat of the burner until the residue is completely white. The first gentle heating decomposes organic substances, driving off all volatile matter and leaving a residue of carbon and the

inorganic constituents of the sample. At a bright cherry-red heat, the calcium carbonate decomposes to carbon dioxide and calcium oxide. The carbon dioxide unites with the residual carbon, forming carbon monoxide which burns off, leaving a white ash. The characteristic blue flame of carbon monoxide can be seen playing over the surface of the mass in the crucible.

After the crucible has cooled, transfer its contents to a 250-cc. beaker. Moisten the ignited material with 25 cc. of water. Rinse the crucible first with water, then with dilute nitric acid, and again with water, adding the washings to the beaker. Then cautiously add dilute nitric acid with stirring until all the material in the beaker has dissolved. Add 3 cc. of nitric acid in excess. At this time, if the amount of dehydrated silica is large, it should be filtered. If it is small, it does not interfere in the subsequent operations. Then prepare the solution for the precipitation of phosphorus according to any of the usual methods, depending on the formation of ammonium phosphomolybdate. The time required from weighing out the sample until the solution is ready for precipitation is usually from 25 to 35 minutes.

TABLE III. COMPARATIVE PHOSPHORUS CONTENT OF AIR-DRIED GROUND SOY BEAN SEED BY TWO METHODS

(1-gram sample used in magnesium nitrate method; 2-gram in calcium carbonate)						
SAMPLE	MAGNESIUM NITRATE METHOD KOH (1 cc. ≈ 0.000207 Gram P)			SAMPLE	CALCIUM CARBONATE METHOD KOH (1 cc. ≈ 0.000207 Gram P)	
	Cc.	Gram	%		Cc.	Gram
1	33.2	0.0069	0.69	67.8	0.0140	0.70
2	33.1	0.0069	0.69	69.5	0.0139	0.72
3	33.2	0.0069	0.69	67.2	0.0139	0.70
4	34.2	0.0071	0.71	66.8	0.0138	0.69
5	34.6	0.0072	0.72	67.2	0.0139	0.70
6	32.5	0.0067	0.67	65.7	0.0136	0.68
7	33.2	0.0069	0.69	68.0	0.0141	0.70
Av.			0.693	Av.		
Std. devn.			0.015	Std. devn.		

TABLE IV. COMPARATIVE PHOSPHORUS CONTENT OF DRIED GROUND TIMOTHY HAY BY TWO METHODS

(1-gram sample used)						
SAMPLE	MAGNESIUM NITRATE METHOD KOH (1 cc. ≈ 0.000207 Gram P)			SAMPLE	CALCIUM CARBONATE METHOD KOH (1 cc. ≈ 0.000207 Gram P)	
	Cc.	Gram	%		Cc.	Gram
1	9.1	0.0019	0.19	9.3	0.0019	0.19
2	9.2	0.0019	0.19	9.8	0.0020	0.20
3	9.1	0.0019	0.19	9.6	0.0020	0.20
4	9.1	0.0019	0.19	10.0	0.0021	0.21
5	9.7	0.0020	0.20	10.0	0.0021	0.21
6	10.0	0.0021	0.21	9.9	0.0020	0.20
7	9.5	0.0020	0.20	10.0	0.0021	0.21
8	9.2	0.0019	0.19			
Av.			0.195	Av.		
Std. devn.			0.007	Std. devn.		

In order to determine the accuracy of the phosphorus determination using this method of ashing, several experiments were carried out. First, a series of blanks containing only the same amount of calcium carbonate as used in the determination were treated with varying known amounts of phosphorus in a standardized solution of microcosmic salt. The water was evaporated, the crucibles ignited, and the analysis carried out as described above. In each case the ammonium phosphomolybdate was thrown down at

¹ This method has been in use in this laboratory during the past 2 years. After completion of the present manuscript, the following note concerning a method using calcium carbonate for ashing plant samples came to the attention of the authors: Lepper, W., *Landw. Vers.-Sta.*, **111**, 159 (1930).

65° C., digested a half hour at that temperature, filtered, washed, and titrated. The purpose of this experiment was to determine if the large amount of calcium nitrate in the solution affects the recovery of phosphorus. The data are given in Table I. The small deviations in this table show that the various substances in the solution have no appreciable effect on the determination of the phosphorus present.

In order to compare the results obtained by the calcium carbonate method with those obtained by the standard magnesium nitrate method, a series of phosphorus determinations were made by each method on samples of dried

corn blades, ground soy bean seed, and dried ground timothy hay. The results of these analyses by the two methods are given in Tables II, III, and IV. It is apparent from these data that the calcium carbonate method is not only comparable in degree of accuracy with the standard magnesium nitrate fusion, but is also adapted for use with widely different types of plant material. No difficulties in manipulation were encountered in the calcium carbonate ashing of any of the three different plant materials used, even though they differ widely in physical and chemical properties.

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Determination of Substantivities of Dyes

A General Method

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THE term "substantivity," introduced originally by Bancroft in 1794 to distinguish a class of dyes, has gradually come to describe the attraction which exists between a dye in solution and a fiber of certain colors. This attraction does not appear to be similar to chemical affinity, but, on the contrary, in recent years dyeing has been classed as an adsorption phenomenon. Later in this paper it will be seen that the form of the curves obtained confirms this point of view. It is well known that for a particular class of fiber some dyes exhibit a greater affinity than do certain others.

For instance, in dyeing the vats Jade Green and Yellow G together by the exhaustion method in a beaker, the latter color does not attach itself to the fiber to any great extent until the Jade Green is largely exhausted from the solution. Rough approximations of relative attraction, in the case of dyes coloring cellulose, may be made by placing drops of solutions upon filter paper. In such cases, the dyed circle so produced is small where the attraction is great, and vice versa; whereas the water ring surrounding the dyed circle is correspondingly wide or narrow.

To obtain data relative to the speed of adsorption, it is possible, by dyeing a series of pieces successively in the same dye bath each for the same fixed period of time, to obtain an idea of the adsorption characteristics of a dye.

With the advent of synthetic fibers, this divergence in speed of application became so magnified as to lead Whittaker (3) to classify colors according to substantivity, giving to each a number designed to express its relative speed of attachment. Thus those dyes, having the same numbers, attach themselves to fibers at similar speeds.

Although each of the above methods affords a means of classifying dyes in accordance with their substantivities, it does not appear that a sufficiently accurate general method is so provided as to lead to a broad understanding of the adsorption phenomena of dyes. At the present time it is generally thought that very finely dispersed particles act in solution as

THIS PAPER describes a general method for obtaining the adsorption curve of any dyestuff on any fiber. Results have been procured by using the skin-friction machine to obtain a set of dyeings made at known concentrations. A long tapering dyeing is then made under constant conditions, except that the dye is gradually exhausted. A comparison is made of the two sets of dyeings on the General Electric recording spectrophotometer. An integration leads to a final curve which, for its characteristic portion, is a straight line on log paper. Varying conditions of temperature, mercerization, speed, tightness of twist, and the like throw the curve either up or down but do not change its angle.

if they were molecules. If this is the case, we should accordingly expect the adsorption characteristics of a dye solution to vary in accordance with concentration. A reliable general method must take this last circumstance into consideration, because the attraction between a certain fiber and a dye in solution at one concentration is not necessarily the same at a different concentration. The method to be described is designed to cover the range of concentrations, which may be designated as the range of true solution.

In exhaustion dyeing, where an end point or at least an equilibrium may be reached, adsorption data are highly desirable and useful. In continuous machine dyeing such data become a necessity. Here an equilibrium is never reached. White cloth is continuously entering the dye bath and dyed cloth is continuously leaving it. If the constitution of the dye bath changes, the shade so produced also changes. To prevent such changes, amounts of dyes equal to those removed by the cloth must be continuously fed into the dye bath in order to maintain a constant concentration.

The continuous application of sulfur colors to cotton cloth has been carried on successfully in this country for a number of years. In this case, the formulas of the make-up solutions have been worked out empirically. Because of the inferior tinctorial value of this class of colors, together with a low substantivity, the problem here is unusually simple. Direct dyes, vats, and acid colors present an increasing order of substantivity. As a result of studies upon the continuous application of these colors to various fibers, the desirability of reliable adsorption data became apparent, and a general method for obtaining them has been worked out.

This method consists in determining and comparing the weights of various dyes which attach themselves to woven fibers in a unit period of time under control conditions. It is apparent that the mere immersion of a sample in a dye solution is not likely to yield satisfactory or accurate results. By keeping the immersed sample in motion better results are

obtained. The method under discussion, which is more rapid in operation and uniform in result, consists in producing an active and uniform circulation of the dye solution through the sample. Determinations of the amounts of dye adsorbed in a unit period of time are made by the spectrophotometer.

LABORATORY MACHINE USED

Any systematic attempt to arrive at a general method for determining the adsorption characteristics of dyes requires, in the first place, an accurate and consistent means of applying dyes to the desired fiber at any practical concentration. In

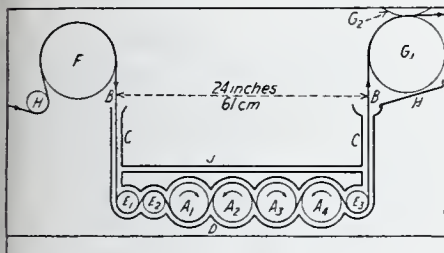


FIGURE 1. CROSS SECTION OF MODEL E LABORATORY MACHINE

the second place, there must be available a reliable means of accurately measuring the amount of color adsorbed in the dyeing operation. The absence of such convenient instrumental means has hitherto retarded, on the one hand, a systematic study of ad-

sorption data as applied to dyes, and, on the other, has prevented the art of dyeing from becoming truly scientific. As a means of dyeing standard cloth in any desired concentration of dye solution, a regular laboratory commercial model of the skin-friction machine (Figure 1), devised, by one of the authors, has been used. As this machine has been described elsewhere (2), only a brief explanation of the principle involved in its use is necessary here. It is well known that when a submerged or partially submerged solid is moved through a liquid, there is set up in the liquid a corresponding current which follows the travel of the solid. Such motion of the liquid is called a skin-friction current. In the adaptation of this principle to dyeing, the solid takes the form of a number of driven cylinders submerged in a solution of the dye, and the cloth to be dyed passes under and over successive rolls, as shown in Figure 1. When the rolls are revolved, a portion of the dye solution follows them in the form of a

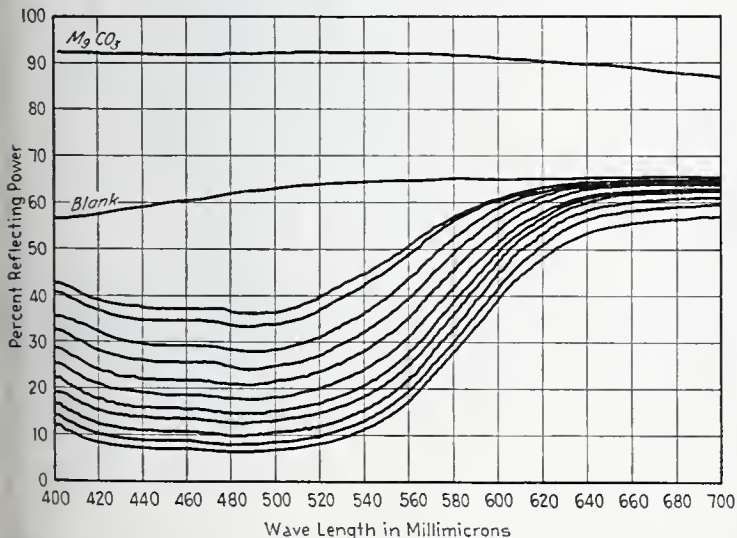


FIGURE 2. COLOR ANALYZER CURVES OF KNOWN-CONCENTRATION SERIES

skin-friction current. This current travels at high speed and possesses corresponding kinetic energy. Where it meets the cloth, partially lapping the roll, it tends to carry on through the cloth, so that the total effect is like a series of pumps driving the dye solution continuously through the cloth and between the fibers. The whole virtue of the arrangement consists in

the positive circulation of dye solution through the fabric many times during the period of contact. In this respect it differs from most other dyeing machines which merely involve the pulling of cloth through dye solutions.

This laboratory model has all the dimensions of full-scale operation except width. By the use of it, dyeings on narrow strips of cloth, usually 2.5 or 3 inches (6.35 or 7.62 cm.) in width, may be made at concentrations which may be varied from the lowest likely to be used in practice up to the limits of solubility. Temperatures may be maintained at any desired point up to the boiling point of water. The strips to be dyed pass through the machine at the rate of 60 yards (54.8 meters) per minute, so that the period of contact between a given part of the strip and the dye solution is slightly in excess of 1 second. The volume capacity of the machine is 3500 cc. The driven rolls are 3.25 inches (8.25 cm.) in diameter, and revolve at a speed of 1740 revolutions per minute.

Measurements of the color value of dyeings produced by the above means have been made on the General Electric recording color analyzer, devised and described by Hardy (1). Readings of samples have been made by the laboratory staff of Cheney Brothers, South Manchester, Conn. Of course, other methods of making these color measurements are now available. The convenience of a recording instrument has facilitated the work greatly and the accuracy of the readings has proved to be sufficient for the purposes of the investigation.

PROCEDURE IN DETAIL

The successive steps in this method are as follows:

- 1. The making of a series of dyeings in which the concentration of the dye bath is known.
- 2. The making of a successive series of dyeings of decreasing intensity in such a way that the amount of dye adsorbed by a known weight of cloth is known.
- 3. Determination of the total light absorbed by each member of the above two series.
- 4. Calculation and plotting of the data obtained in the previous three steps.

KNOWN-CONCENTRATION SERIES. The first step to obtain data on any chosen dye consists in making on strips of standard cloth a series of short dyeings through the machine

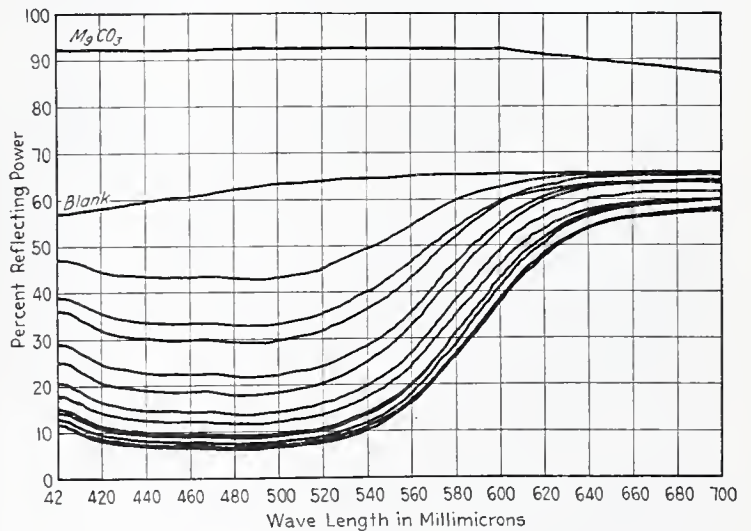


FIGURE 3. COLOR ANALYZER CURVES OF KNOWN-WEIGHT SERIES

in which is placed a series of dye solutions of known concentration. Temperature, roll speed, cloth speed, cloth tension, and chemical concentration are held constant for the entire series. Owing to the fact that between the weight of dye attached to the cloth and the color intensity thereby produced there exists a logarithmic ratio, the following percentages of dye are

usually employed in the solution: 4, 2, 1, 0.5, 0.25, 0.125, 0.0625, 0.03125. Such a series exhibits all ranges of depth usually seen in commercial practice and varies from a heavy shade to a very slight tint. During the passage of the cloth through the machine, the skin-friction currents generated by the driven rolls are continuously circulating between the

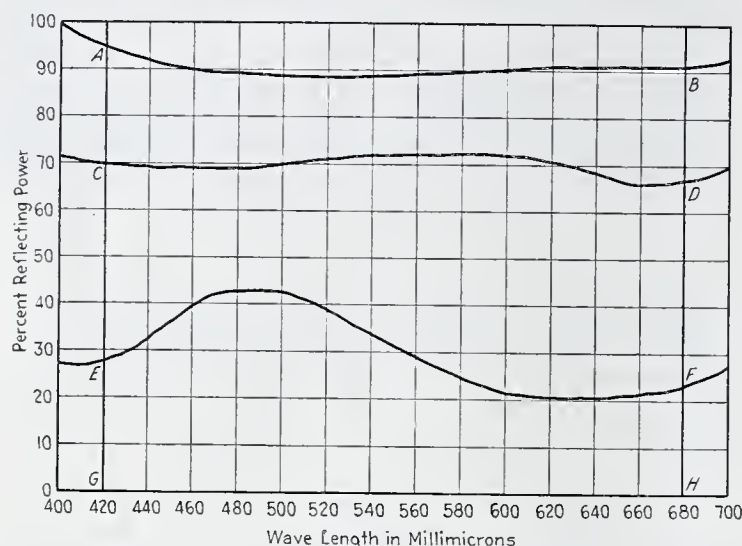


FIGURE 4. SIMPLE COLOR-ANALYZER CURVE

fibers. So effective is this circulation in the typical case that it leaves upon the cloth a higher percentage of dye than was present in the solution through which it passed.

At this stage we are in a position, after color measurement, to plot a dyeing curve through the range of the above concentrations, if the dyeings made as above can be compared with a series of dyeings wherein definitely known weights of dye are attached to the fiber. Such a curve will show known weights of dye adsorbed on one axis and the corresponding concentration of solution used on the other. Unfortunately, pot dyeing, except in specific cases, is too inaccurate for use as a general method.

KNOWN-WEIGHT SERIES. Comparing the adsorption rate of two dyes by dyeing a long strip through a solution of each of the dyes, thus exhausting them while maintaining a constant volume, it is evident that exhaustion will take place more quickly in the case of the more substantive dye. Consequently, the lengths—or weights—of the strips so dyed in obtaining exhaustion will afford a measure of relative substantivity or adsorption rate.

This principle is used in the preparation of the known-weight series. The procedure is to make a long dyeing which passes in intensity of shade through all percentages of the known-concentration series. As it is made, this dyeing changes by infinite variation from the strongest to the weakest member of the known-concentration series. A solution corresponding to the highest concentration of the above series is put into the machine. A constant volume is maintained by using a Mariotte bottle containing water and proper proportions of caustic soda and sodium hydrosulfite in the case of vat colors, but containing no dye. Temperature, speed, and all other conditions are constant. As the cloth passes through the solution, adsorption deprives the solution of dye, and consequently the dyeing so produced becomes weaker and weaker until finally the cloth passing through the machine is only slightly tinted.

Subsequent to customary after-treatment, the long strip so produced is sampled by taking out a strip at the entering end and thereafter at successive 500-gram lengths. The set of samples thus taken is called the known-weight series.

By referring the members of the series so produced colorimetrically with the known-concentration series we have a possible method of arriving at the rate of adsorption, since by

a colorimetric comparison we arrive at an idea concerning the weights—or lengths—of cloth upon which a definite weight of dye was adsorbed in a definite time.

COLOR RECORDS. Each series is now ready for the color analyzer. The procedure followed is to record each series on a single sheet of graph paper which shall show, in addition, a record from a block of magnesium carbonate and from a blank piece of the cloth on which both series were dyed. An examination of the accompanying color-analyzer curves, Figures 2 and 3, makes it clear that there is a significant and expected parallelism between the different members of a series. Any deviation is at once apparent and may be checked and repeated. Errors in manipulation are fortunately easy to detect at this stage or later.

PLOTTING OF SERIES. For purposes of estimation, it is apparent that the needed data shall include all color values in the visible spectrum. Referring to Figure 4, the curve *AB*, recording the light reflected from a plane surface of magnesium carbonate, represents for our purposes 100 per cent reflection and is the standard. The line *CD* records the light reflected from the undyed cloth in the blank, and the line *EF* records the light reflected from the dyed sample. In the calculations the light reflected between $\lambda 400$ and $\lambda 420$ and between $\lambda 680$ and $\lambda 700$ has been discarded. It therefore follows:

Area *AGHB* = light reflected from magnesium carbonate

Area *CGHD* = light reflected from blank

Area *EGHF* = light reflected from sample

Area *AGHB* — area *CGHD* = absorption of light by blank

Area *CGHD* — area *EGHF* = absorption of light caused by dye applied to blank, which is area *CEFD*

The most simple method of determining these areas consists in running a planimeter carefully around them.

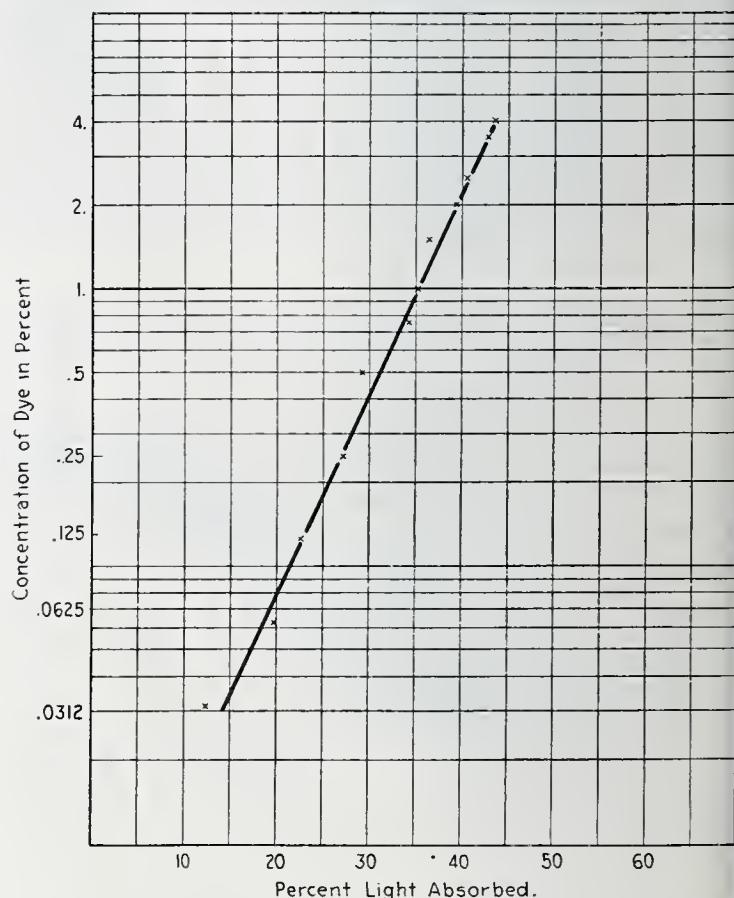


FIGURE 5. CURVE I

To find the percentage of light absorbed by a sample, the area under the sample is subtracted from the area under the blank and divided by the area under the magnesium carbonate thus:

$$100 \times \frac{\text{area } CGHD - \text{area } EGHF}{\text{area } AGHB} = \text{percentage absorption}$$

The color-analyzer curves for each of the two series (Figures 2 and 3) are thus measured and the percentage of light absorption of each sample recorded in tabular form. From these data two curves are now plotted. Figure 5 (Curve 1) illustrates the type of curve obtained by plotting the data of the

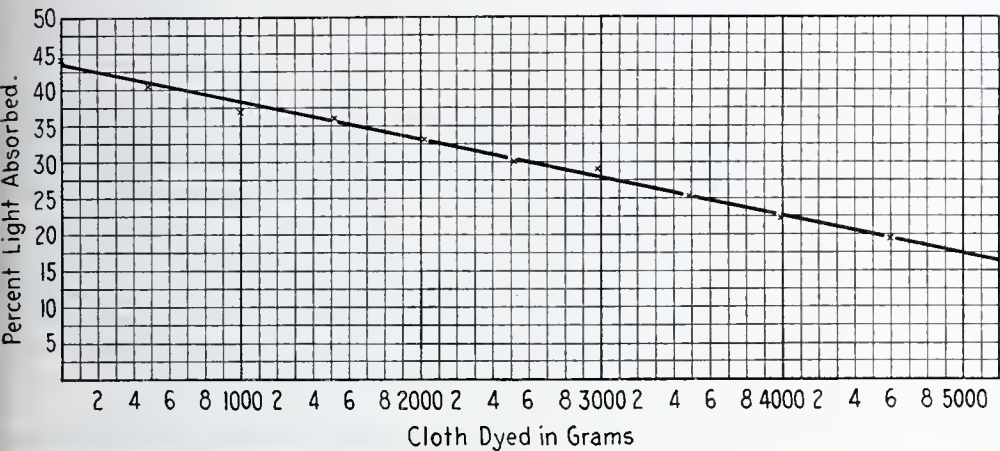


FIGURE 6. CURVE II

known-concentration series, where the y axis denotes the concentration of the dye solution in per cent, and the x axis the per cent light absorption as recorded. Similarly, in Figure 6 (Curve II), for the known-weight series we have weights of cloth run out plotted against the percentage of light absorption of the samples.

When a particular dye is applied to the same cloth under the same conditions, it is reasonable to conclude that identical color effects must be produced by identical weights of adsorbed dye. We are, therefore, in a position to know from the data of Curve I how much dye was adsorbed by a weight of cloth between any two points on Curve II by referring to the common standard of light absorption. It is more convenient, however, to plot a new curve (Figure 7, Curve III) which shows on the y axis percentage concentration of dye solution, and on the x axis the weight of cloth run out in grams.

It is at once apparent that from Curve III may be derived some real quantitative information. For instance, on any part of the curve the drop in concentration which took place while 100 grams of cloth were dyed and, therefore, the weight of dye adsorbed by that 100 grams of cloth, may be found. As the color is gradually tapering, there must be some way of determining the mean adsorption. To do this it is necessary to proceed by a series of infinitesimals. Referring to Curve III, if the assumed points y_4 and y_3 are taken, and the corresponding points x_4 and x_3 cut off on the x axis,

$$\Delta y = y_4 - y_3, \text{ and } \Delta x = x_4 - x_3$$

while Δy = percentage of dye in the bath used on Δx grams of cloth. As the volume of the bath is 3500 cc., $\Delta y \times 3500$ = grams of dye used on Δx grams of cloth. Therefore,

$$\frac{\Delta y \times 3500}{\Delta x} = \text{average weight of dye used on 1 gram of cloth for interval } x_3 - x_4, \text{ and so for any other part of the curve.}$$

Transferring a series of these results to a new curve (Figure 8) where the y axis is the weight of dye on 1 gram of cloth and the x axis the weight of the cloth dyed, the rectangle $PQRS$ represents the weight of dye used on $(R - Q) = \Delta x$ grams of cloth. In this way a series of small rectangles may be made which represent the actual dye used on the cloth run out. If the top of these rectangles is divided in half at the points C, D , and E , and joined by a curve, then the area under the curve AB represents the amount of dye applied to Δx grams of cloth run out, for, as the curve AB is short, it is to all intents a straight line, and as the triangle APC is equal to the triangle CSB , the area under the curve AB is equal to the area of the rectangle $PQRS$.

The values obtained for a large number of middle points, when tabulated, enable us to plot Curve IV (Figure 9), wherein on the x axis is given the concentration of the dye solution in per cent, whereas on the y axis is given the percentage weights of dyes which will be adsorbed on cloth when dyed under the conditions present when the two known series were dyed. These conditions are usually arranged so as to provide usual and average workability for the dyes of the class into which each comes. It will be understood that these conditions for direct colors, for instance, would vary from those to be employed in the case of vats or acid colors.

USE OF DATA

In practice, the curves serve a necessary purpose. When a sample is matched on the laboratory machine, the percentage of each dye present is known. Reference to the curve of each dye tells at once how much dye must be fed into the machine to compensate for that taken out by the cloth, and a dye bath is made up accordingly. Conversely, if it is known what dyes and how much of them were used to produce the shade exhibited by a particular sample, reference to the curves will give the needed percentage of those same dyes to be used in the starting bath. The feed in this case will be the amount of

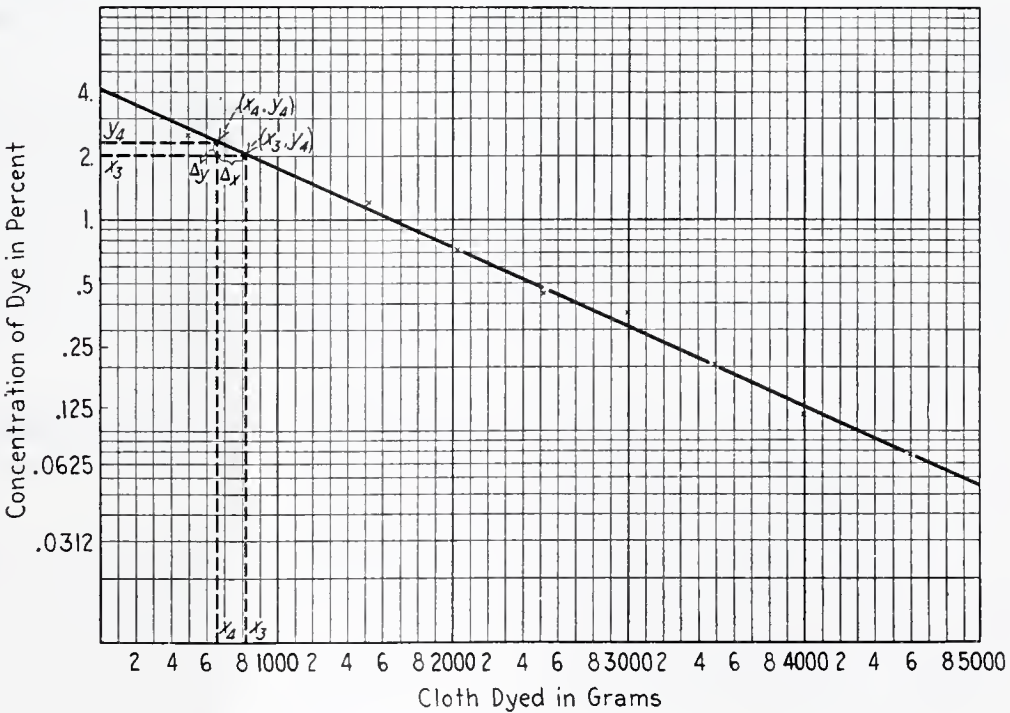


FIGURE 7. CURVE III

dyes which have been found necessary to produce the shade on the sample.

In exhaustion dyeing, a study of these curves proves of practical utility, because it is evident that dyes whose curves have a like or nearly like locus will exhaust at an equal or

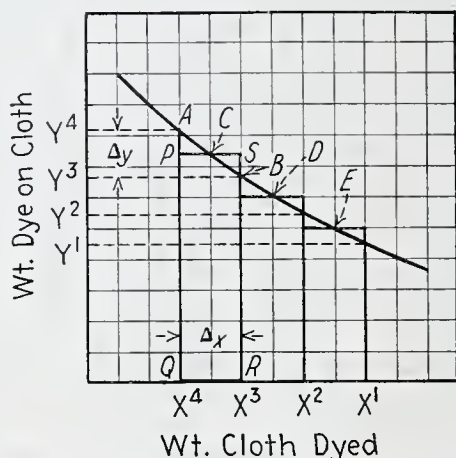


FIGURE 8. SMALL SECTION OF CURVE REPLOTTED FROM CURVE III

nearly equal rate, as the case may be. Such dyes give the best working conditions when used together. Even when the curves of dyes differ widely, they sometimes cross each other. In this case it is apparent that if dyeing conditions are adapted to correspond to this point of crossing, the dyes will work together well.

CURVES AS EXPRESSION OF PROPERTIES

The form which Curve IV exhibits makes it apparent at once that no chemical action is indicated between the dye and the fiber constituting the cloth. The equation for a curve of this locus is

$$y = cx^n$$

where y = percentage of dye adsorbed
 x = percentage of dye in solution
 n = tangent the curve makes with horizontal axis
 c = variables

The common variables are time, temperature, roll speed, hydration (mercerization), tightness of twist and weave, and hydrogen-ion concentration.

So far as observations extend, the angle of the curve, expressed by the exponent n , represents the essential characteristics of an individual dye, and this angle is not changed by the variables. This is only true, however, in so far as it represents the adsorption characteristics of a dye for a single class of fiber. Up to date there has been little opportunity to prepare curves of the same dye for different fibers.

Although the variables do not appear to influence the value of the exponent n , they do, of course, change the position of the curve, throwing it either up or down. Thus an increase in time, temperature, or roll speed elevates the curve, whereas an increase in tightness of twist or weave depresses it.

By reference to the curves on Figure 9, it will be seen that A for Golden Orange 4R makes a 45-degree angle with the base. In this case the exponent in the equation, $y = cx^n$, becomes unity and the curve would be a straight line if plotted on ordinary coördinate paper. It would appear, therefore, that in such case the adsorption varies lineally with the concentration. In other cases illustrated (Figure 9,

B, C, and D), the angle made is less than 45 degrees and as a consequence the adsorption is no longer a lineal function of the concentration. Although the extreme ends of these curves have not been studied intensively, it seems probable that at either end the curve tends to become parallel with the base. All these observations suggest a number of questions which can be answered only after further studies have been made.

Of the many questions which arise, the following may be chosen:

1. When the angle of the curve is 45 degrees, do we have a perfect solution in which the adsorption (for a particular fiber) becomes a function of the number of molecules present or of the number of particles present so finely dispersed as to behave like molecules?
2. When the angle of the curve is less than 45 degrees, do we have a case of imperfect dispersion and, if so, is adsorption a direct function of the proportion of finely dispersed particles actually present in a solution of given concentration?
3. How is the locus of an adsorption curve determined by the molecular weight and structure of the solute?

It is evident that in the course of this work there have been accumulated considerable data expressing definitely the relationship between color value and weight of adsorbed dye producing it. Once this relationship in a group of colors has been determined, the next logical step is to determine the final color value produced when definite weights of two or more

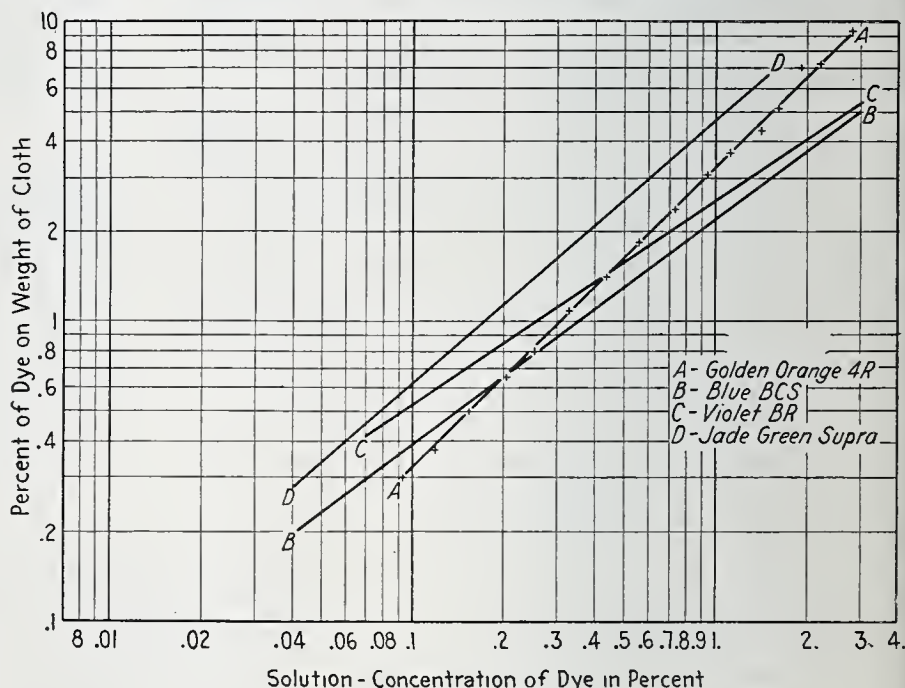


FIGURE 9. CURVE IV

of the group are dyed upon the same fibers. This interesting question will be the subject of a future paper.

ACKNOWLEDGMENT

It gives the authors much pleasure to record their gratitude to Cheney Brothers for valuable assistance in reading samples of color measurements.

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Determination of Sulfur in Urine

Rapid Photometric Method

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IN A recent paper by Toepfer and Boutwell (11), the use of the sulfur photometer for the rapid determination of sulfur in foods and biological materials is described. It was thought that if this method could be successfully applied to the determination of the distribution of sulfur in urine, it should offer advantages over the usual method in speed and ease of operation. It is the purpose of this paper to describe such a photometric method together with a method for the oxidation of the sulfur for the determination of total sulfur.

Jackson (6) and, in earlier papers, Hinds (5) describe the use of a crude photometer for the determination of sulfates. Both authors refer to the application of their method to the rapid estimation of inorganic sulfates in urine. The use of the photometer in the determination of sulfur in coal is described by Parr and McClure (9). The sulfur photometer has been improved and placed on the market as the "Burgess-Parr Sulfur Photometer." In the directions (2) for its use, its application to the determination of sulfur in foods is given, following the oxidation of the sample with sodium peroxide in the sulfur bomb. In attempting to adapt this method to the determination of total sulfur in urine, a few trials proved that the sodium peroxide bomb fusion was not suited for the oxidation. Benedict's (1) method using copper nitrate and potassium chlorate could not be used because of the color of the solution if it was to be followed by the photometric method. Dennis and Reed (3) have avoided this difficulty in their nephelometric method by the substitution of zinc nitrate for copper nitrate in their oxidation mixture. The authors have used a wet method of oxidation in a small Pyrex Kjeldahl flask involving the use of fuming nitric acid and 70 per cent perchloric acid as suggested by LeMatte, Boinot, and Kahane (7) for the oxidation of sulfur in biological material. This method was improved and used successfully with no appreciable loss of sulfur by Wolesensky (12) and by Mackay (8) in the determination of sulfur in rubber. Zahnd and Clarke (13) report the loss of sulfur in the use of nitric and perchloric acids. Their method of carrying out the oxidation differs from the one which the authors (11) have used, wherein no appreciable loss of sulfur in the oxidation of various types of biological material has been experienced. Its application to the oxidation of sulfur in urine has proved successful. After oxidation, the resulting solution is easily prepared for either the gravimetric or photometric determination of sulfates. It should be noted that any error in the precipitation of barium sulfate in the presence of nitric and perchloric acids is avoided by the destruction of the excess of these acids at the end of the oxidation.

The reliability of the photometric method when applied

THE APPLICATION of the sulfur photometer to the rapid determination of sulfur in urine is described. A method involving the use of nitric and perchloric acids has been used in the oxidation of urine for total sulfur and may be followed by either the photometric or gravimetric determination of the sulfur. This method of oxidation, together with the use of the sulfur photometer, possesses advantages in speed and ease of operation, and, in the hands of an experienced operator, offers a reliable and rapid routine method of analysis.

to the determination of small quantities of sulfur in biological material has been confirmed in earlier work (11). In the hands of an experienced operator, the photometer makes possible the determination of sulfates in from 10 to 15 minutes with an error of about 0.03 mg. in 2 to 3 mg. of sulfur, the optimum amount for the determination.

DETERMINATION OF INORGANIC SULFATES

The preparation of the solution for the photometric determination of inorganic sulfates followed essentially the method of Folin (4). Twenty-five cubic centimeters of urine and 10 cc. of 1 to 4 hydrochloric acid were diluted to 250 cc. in a volumetric flask. From this solution an aliquot was taken, usually 25 cc., containing from 2 to 3 mg. of sulfur. To the aliquot were added 25 cc. of salt solution containing 120 grams of sodium chloride per liter. The resulting solution was made up to 100 cc. The colloidal barium sulfate necessary for the photometric determination was formed by the addition of 0.3 to 0.5 gram of sized barium chloride crystals (20 to 30 mesh) and then mixed by shaking. After standing for 5 minutes with occasional shaking, the readings were taken on the photometer. The directions (2) for the use of the instrument were carefully followed. With practice in reading the instrument and under correctly controlled conditions, excellent checks can be obtained.

The photometric results were checked by Folin's (4) gravimetric method, and the comparisons are shown in Table II.

DETERMINATION OF TOTAL SULFATES

For the determination of total sulfates, the urine was hydrolyzed according to Folin's (4) method. Twenty-five cubic centimeters of urine and 20 cc. of 1 to 4 hydrochloric acid were placed in a Pyrex Erlenmeyer flask covered with a small watch glass and boiled gently for 30 minutes. The solution was cooled, transferred to a 250-cc. volumetric flask, and the contents made up to volume. A suitable aliquot was taken, usually 25 cc., containing about 2 to 3 mg. of sulfur. To this were added 25 cc. of a salt solution containing 3 grams of sodium chloride, the volume made up to 100 cc., and the photometer readings made as before. The results were checked by the usual gravimetric method (4). The comparisons are shown in Table II.

In the course of the hydrolysis of the ethereal sulfates with hydrochloric acid, there is a gradual darkening of the urine. It was first thought that this darkening would make the solution unfit for photometric determinations. The color fades out considerably on dilution and does not affect the accuracy of the readings. This was shown by adding known amounts of a standard solution of potassium sulfate to a solution of hydrolyzed urine prepared as described above in which the total sulfates had been determined, and noting the recovery of sulfur obtained. The results are given in Table I.

¹ Since the completion of this paper, the form of the photometer has been simplified to increase its speed and accuracy and renamed the "Burgess-Parr Turbidimeter." The new form is now being used in this laboratory in preference to the old in the continuation of our work.

TABLE I. PHOTOMETRIC RESULTS FOR TOTAL SULFATES UNAFFECTED BY DARKENING OF HYDROLYZED URINE

SULFUR IN SOLN. TAKEN	SULFUR ADDED	SULFUR PRESENT	SULFUR FOUND	ERROR	SULFUR RECOVERED
Mg.	Mg.	Mg.	Mg.	Mg.	%
0.812	1.000	1.812	1.82	+0.008	100.44
0.812	1.200	2.012	2.03	+0.018	100.89
0.812	1.400	2.212	2.35	+0.138	106.22
0.812	1.600	2.412	2.41	-0.002	99.91
0.812	1.800	2.612	2.66	+0.048	101.83
0.812	2.000	2.812	2.83	+0.018	100.64
0.812	2.200	3.012	3.04	+0.028	100.92

TABLE II. COMPARISON OF PHOTOMETRIC AND GRAVIMETRIC RESULTS FOR INORGANIC SULFATES, TOTAL SULFATES, AND TOTAL SULFUR

SAMPLE	DETERMINATION	METHOD	VOL. IN ALI-QUOT		WT. OF BaSO ₄	WT. OF S	WT. OF S PER LITER	AV. S PER LITER
			Cc.	Cc.	Gram	Mg.	Gram	Gram
1	Inorg. SO ₄	Photo.	25	2.5		1.78	0.712	
		Photo.	25	2.5		1.78	0.712	0.712
		Grav.	25		0.1303	17.90	0.716	
		Grav.	25		0.1288	17.70	0.708	0.712
	Total SO ₄	Photo.	25	2.5		1.91	0.764	
		Photo.	25	2.5		1.91	0.764	0.764
		Grav.	25		0.1372	18.84	0.754	
		Grav.	25		0.1365	18.72	0.749	0.752
	Total S	Photo.	5	2.5		2.06	0.824	
		HClO ₄	5	2.5		2.06	0.824	
			5	2.5		2.06	0.824	0.824
		Grav.	10		0.0592	8.13	0.813	
		HClO ₄	10		0.0588	8.08	0.808	0.811
		Grav.	10		0.0606	8.32	0.832	
		Benedict	10		0.0616	8.46	0.846	0.839
2	Inorg. SO ₄	Photo.	25	3.5		2.17	0.620	
		Photo.	25	3.5		2.17	0.620	0.620
		Grav.	25		0.1152	15.82	0.633	
		Grav.	25		0.1152	15.82	0.633	0.633
	Total SO ₄	Photo.	25	3.5		2.41	0.688	
		Photo.	25	3.5		2.39	0.683	0.685
		Grav.	25		0.1242	17.06	0.682	
		Grav.	25		0.1232	16.92	0.677	0.680
	Total S	Photo.	5	2.5		1.83	0.732	
		HClO ₄	5	2.5		1.84	0.736	
			5	2.5		1.82	0.728	0.732
		Grav.	5		0.0275	3.78	0.755	
		HClO ₄	5		0.0268	3.68	0.736	0.746
		Grav.	10		0.0572	7.86	0.786	
		Benedict	10		0.0558	7.66	0.766	0.776
3	Inorg. SO ₄	Photo.	25	3.5		2.08	0.594	
		Photo.	25	3.5		2.06	0.588	0.591
		Grav.	25		0.1076	14.78	0.591	
		Grav.	25		0.1076	14.78	0.591	0.591
	Total SO ₄	Photo.	25	3.5		2.18	0.622	
		Photo.	25	3.5		2.18	0.622	0.622
		Grav.	25		0.1165	16.00	0.640	
		Grav.	25		0.1160	15.93	0.637	0.638
	Total S	Photo.	5	3.75		2.47	0.659	
		HClO ₄	5	3.75		2.47	0.659	0.659
			5		0.0249	3.41	0.683	
		HClO ₄	5		0.0242	3.32	0.664	0.673
		Grav.	10		0.0490	6.73	0.673	
		Benedict	10		0.0488	6.70	0.670	0.671

DETERMINATION OF TOTAL SULFUR

For the determination of total sulfur, 5 cc. of urine were measured into a 300-cc. Pyrex Kjeldahl flask by means of an Ostwald pipet, and 2 cc. of fuming nitric acid (sp. gr. 1.50) and 1 cc. of 70 per cent perchloric acid were added. The solution was heated carefully over a low flame until the first reaction had practically ceased. It was then boiled gently until white fumes appeared. At this point the solution should be colorless or nearly so. If not, more perchloric acid was added and the boiling continued. The solution was then cooled and 2 grams of sodium chloride were added. This released chlorine and nitrogen dioxide from the destruction of the excess of nitric and perchloric acids. The flask was heated until the evolution of the fumes had ceased and the solution was colorless. It was then diluted with 20 to 30 cc. of water and made just basic with 4 N sodium hydroxide, then neutralized and made acid with 1 cc. in excess of concentrated hydrochloric acid. This treatment insures the correct salt content and acidity for the subse-

quent photometer determination. The solution was made up to 100 cc. and suitable aliquots were taken for the photometer readings. The oxidations can be completed and the solutions prepared for the readings in from 1 to 1.5 hours. A blank for the perchloric acid method of oxidation was determined according to the "true blank" method of Stockholm and Koch (10). The blank was equivalent to 0.002 gram of barium sulfate or 0.28 mg. of sulfur, for which the corresponding results in Table II have been corrected. The results for total sulfur were checked in two ways. First, they were compared with gravimetric determinations made on the solution following the perchloric acid oxidation of the urine. Second, both the photometric and gravimetric results following the perchloric acid oxidation were compared with the results obtained by Benedict's (1) gravimetric method. Blank determinations were made for Benedict's method by the true blank method. The blank averaged 0.0044 gram of barium sulfate, for which the corresponding figures in Table II have been corrected.

The comparative results shown in Table II were all made on 24-hour samples of urine. The volumes were made up to 1000 cc. in each case. The results are calculated to grams of sulfur per liter and represent the output of inorganic sulfates, total sulfates, and total sulfur for the 24-hour periods.

RETENTION OF SULFUR IN PERCHLORIC ACID METHOD OF OXIDATION

In order to see if there was any loss of sulfur during the perchloric acid method of oxidation, aliquots of a urine of known total sulfur content were oxidized, and the per cent of sulfur recovered after correcting for the blank was determined. The results which are given in Table III show that there is no apparent loss of sulfur during the oxidation in the Kjeldahl flasks.

TABLE III. PHOTOMETRIC DETERMINATIONS SHOWING RETENTION OF SULFUR DURING PERCHLORIC ACID OXIDATION

TOTAL S PRESENT	TOTAL S FOUND	ERROR	S RECOVERED
Mg.	Mg.	Mg.	%
2.15	2.16	+0.01	100.4
2.15	2.17	+0.02	100.9
2.15	2.15	0.00	100.0
2.15	2.15	0.00	100.0
2.84	2.87	+0.03	101.0
2.84	2.85	+0.01	100.3
2.84	2.84	0.00	100.0
2.84	2.84	+0.01	100.3
2.65	2.66	+0.01	100.2
2.65	2.62	-0.03	98.9
2.65	2.62	-0.03	98.9
2.65	2.67	+0.02	100.7

APPLICATION OF METHOD TO ROUTINE ANALYSIS

The photometric method was tried out on a series of 24-hour samples of urine with the results shown in Table IV, expressed in grams of sulfur per 24-hour period. The usual diet, which was rather low in protein, was observed throughout except that for April 16, the diet was high in sulfur and for April 27 it was somewhat higher in protein. The data have small interest aside from showing the consistency of the results which may be expected by this method.

TABLE IV. NITROGEN CONTENT AND SULFUR DISTRIBUTION

DATE OF SAMPLE	TOTAL N	INORGANIC SO ₄	TOTAL SO ₄	TOTAL S	ETHEREAL SO ₄	NEUTRAL S
	Grams	Gram	Gram	Gram	Gram	Gram
April 15	...	0.304	0.354	0.436	0.050	0.082
April 16	11.44	0.814	0.893	1.030	0.079	0.127
April 17	10.77	0.732	0.840	0.928	0.108	0.088
April 18	11.57	0.681	0.849	0.936	0.168	0.087
April 24	9.77	0.550	0.596	0.658	0.046	0.062
April 27	13.10	0.486	0.566	0.664	0.080	0.098

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Emulsive Capacity of Sulfonated Oils

Miscibility of Sulfonated Oils and Neutral Oils

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SULFONATED oils find varied and extensive application in the industries, being used as mordants, dye assistants, detergents, softeners, wetting-out agents, etc. They are particularly useful to the manufacturer of specialty oils for making soluble or emulsifying immiscible liquids, such as fatty oils, mineral oils, and solvents. Many bleach or kier oils on the market are mixtures of sulfonated oil and pine oil or another solvent; wool, silk, and rayon oils are often mixtures of sulfonated oil and mineral, neat's-foot, olive oil, or a similar lubricant. Sulfonated oil also forms the base in the so-called soluble cutting oils for metals, and finally sulfonated cod or other fish oil is used considerably in treating leather.

The emulsifying property of sulfonated oils depends to a great extent upon the nature of the raw oil, method of sulfonation, neutralization of the finished product, moisture content, etc. Geronazzo (2), in discussing leather oils, states that the quality of a sulfonated oil is related directly to the duration of its own emulsion and to its "emulsive capacity"—i. e., the property of retaining a definite quantity of another fatty substance in a homogeneous emulsion. Bumcke (1) concludes that sulfonated oils with the greatest carrying capacity for mineral oils give the best results in practice. In spite of its evident importance there seems to be no detailed procedure in the literature for determining the emulsifying capacity of sulfonated oils; hence the simple method outlined in this paper may be timely. This test is of importance not only in formulating commercial products, but is useful also as a criterion of the quality of the oil and as a means of identification.

A sulfonated-oil mixture to be marketable must be uniform and clear and remain so indefinitely. It has also been found that a clear oil gives a better emulsion than a cloudy product, which may separate on standing. Homogeneity is usually attained by adding oleic acid (red oil) to the mixture (3). An excess of oleic acid, however, must be avoided as it may exert a

THE EMULSIVE CAPACITY of a sulfonated oil is determined by mixing it with various amounts of olive oil, clearing with oleic acid, and finally testing the stability of the emulsion. The emulsive capacity is useful in formulating commercial products, and serves also as a criterion of quality and as a means of identification.

Judging by the amount of oleic acid required to produce uniform mixtures, sulfonated oils are more miscible with mineral than with fatty oils, and both fatty and mineral oils are less miscible with sulfonated castor than with sulfonated olive oil. Sulfonated oils are better emulsifiers for mineral than for fatty oils; in this respect, acid sulfonated castor oil is inferior to acid sulfonated olive oil. Complete neutralization of a sulfonated oil decreases its miscibility with neutral oils. Completely neutralized sulfonated oil, with the proper addition of alcohol, is a better emulsifier for mineral oils than the acid oil but is a poorer emulsifier for fatty oils.

de-emulsifying effect upon the mixture.

PROCEDURE

To determine the emulsive capacity, the writer proposes to find the maximum amount of olive oil which, when mixed with 100 grams of the sulfonated oil under examination, gives an emulsion of a definite stability. A mixture of the two oils is usually cloudy but becomes clear upon adding oleic acid. The test consists of two parts: preliminary emulsions, in which the sulfonated oil varies by 10 per cent intervals; and final emulsions, in which the sulfonated oil varies by 1 or 2 per cent of the mixtures.

PRELIMINARY EMULSIONS.

Ten grams of a mixture of the sulfonated oil and olive oil (9 grams and 1 gram, respectively; 8 grams and 2 grams, respectively, etc.) are thoroughly mixed in a 100-cc. glass beaker, using preferably a thermometer as a stirring rod, and titrated at 40° C. with oleic acid until the mixture just turns clear. Next 0.1 cc. of excess oleic acid is added, and a 5 per cent emulsion made, of which 100 cc. are allowed to stand for exactly 2 hours in a 4-ounce oil bottle. The titration with oleic acid is very sharp and sensitive to less than 0.25 per cent of the mixture. A large excess of oleic acid, for reasons already mentioned, must be avoided. After the 2 hours, the emulsions are closely examined and note made of those showing free oil on the surface. With the preliminary emulsions there is no difficulty in separating the good emulsions from the poor ones, as the change is very marked.

FINAL EMULSIONS. Another series of mixtures is now made beginning with the first satisfactory emulsion containing the least amount of sulfonated oil, but instead of 10 grams, a quantity ten times as much is used, or 100 grams. Six mixtures are made, each consecutive one containing 2 grams less of the sulfonated oil. In each case after clearing, 0.5 gram excess of oleic acid is added. Emulsions are made as above, and the first emulsion next to the last one showing free oil is

taken as the end point. Of course, the change in the nature of the emulsions is not so pronounced as in the previous emulsions, but nevertheless is quite distinct, and a 4-gram interval of the sulfonated oil at the crucial point makes the change unmistakable. Table I gives the results obtained in testing a sulfonated olive oil which had an emulsive capacity of 108. The olive oil used was the ordinary denatured oil containing 4.2 per cent free fatty acids; the oleic acid was a straw-colored commercial red oil of low chilling point.

TABLE I. STABILITY OF EMULSIONS OF MIXTURES OF SULFONATED OLIVE OIL AND RAW OLIVE OIL

MIXTURE	SULFONATED OLIVE OIL Grams	RAW OLIVE OIL Grams	OLEIC ACID TO CLEAR Cc.	STABILITY OF EMULSION
PRELIMINARY TESTS				
1	10	0	0.0	Good
2	9	1	0.0	Good
3	8	2	0.0	Good
4	7	3	0.6	Good
5	6	4	1.1	Good
6	5	5	1.6	Good
7	4	6	2.0	Very poor
8	3	7	2.6	Very poor
9	2	8	3.4	Very poor
10	1	9
FINAL TESTS				
11	50	50	16.5	Good
12 ^a	48	52	17.1	Good
13	46	54	17.8	Poor
14	44	56	18.6	Poor
15	42	58	19.8	Very poor
16	40	60	20.8	Very poor

^a End point; emulsive capacity = 52/48 × 100 = 108.

RESULTS WITH VARIOUS OILS

The emulsive capacity of some commercial oils employed for different purposes and determined as above are shown in Table II. Samples with low numbers proved, upon further testing, to be either products of poor quality or compounded oils to which a certain amount of fatty or mineral oil had already been added.

TABLE II. EMULSIVE CAPACITY OF SOME COMMERCIAL OILS

SAMPLE	MANUFACTURER'S DESCRIPTION	EMULSIVE CAPACITY Grams/100 grams sample
1 N	Sulf. olive oil	108
2 R	Sulf. olive oil	100
3 L	Sulf. olive oil	85
4 P	Sulf. olive oil	56
5 D	Sulf. castor oil	61
6 P	Sulf. castor oil	61
7 A	Sulf. neat's-foot oil	42
8 L	Sulf. neat's-foot oil	38
9 D	Silk oil	35
10 H	Silk oil	35
11 E	Silk oil	45
12 N	Silk oil	10
13 F	Rayon oil	45
14 N	Leather oil	150

Repeated tests have shown, contrary to the prevailing notion, that mineral oil is more readily emulsified by sulfonated oils than fatty oils, provided the mixture is first made into a clear, uniform oil. Mineral oil is also the more miscible, as shown by the much smaller quantity of oleic acid necessary to clear. This is shown in Table III, in which mixtures of a concentrated sulfonated olive oil (moisture content, 24.3 per cent; free fatty acids, 19.0 per cent; soap, 6.0 per cent) and a light spindle oil (specific gravity, 0.845; viscosity, 80 sec. Saybolt at 37.8° C.) were cleared with red oil.

Judging by the amount of oleic acid necessary to clear a given mixture, sulfonated castor oil is less miscible with mineral or fatty oils than sulfonated olive, or similar oil. In Table IV is listed a series of mixtures of the two sulfonated oils with olive oil, from which will be observed the much greater quantity of oleic acid required to clear mixtures made with the sulfonated castor oil. Where the olive is replaced by mineral oil, the difference is even more marked, since a good grade of concentrated sulfonated olive oil will mix with min-

eral oil practically in all proportions without any addition of oleic acid, whereas it is always required in the case of sulfonated castor oil, often to the extent of 25 per cent of the mixture. The difference is still further intensified by completely neutralizing the sulfonated oils. The sulfonated castor oil used in Table IV was of good quality, containing about 25 per cent moisture.

TABLE III. OLEIC ACID REQUIRED TO CLEAR MIXTURES (Sulfonated olive oil and mineral oil; sulfonated olive oil and olive oil)

MIXTURE	SULFONATED OLIVE OIL Parts by wt.	MINERAL OR OLIVE OIL Parts by wt.	EMULSIONS		OLEIC ACID TO CLEAR	
			Mineral oil mixtures	Olive oil mixtures	Mineral oil mixtures % in cc.	Olive oil mixtures % in cc.
1	100	0	Good	Good	0	0
2	90	10	Good	Good	0	0
3	80	20	Good	Good	0	0
4	70	30	Good	Good	0	6
5	60	40	Good	Good	0	11
6	50	50	Good	Good	0	16
7	40	60	Good	Very poor	2	20
8	30	70	Fair	Very poor	5	26
9	20	80	Poor	Very poor	6	34
10	10	90	None	...	10	..

TABLE IV. MISCIBILITY OF SULFONATED CASTOR OR SULFONATED OLIVE WITH OLIVE OIL

(Determined by amount of oleic acid required to clear)

MIXTURE Parts	OLIVE OIL Parts	SULFONATED CASTOR OR OLIVE OIL	OLEIC ACID TO CLEAR: Sulf. castor oil mixture %	Sulf. olive oil mixture %
1	0.0	100	0	0
2	10	90	13	0
3	20	80	23	0
4	30	70	28	6
5	40	60	32	11
6	50	50	34	16
7	60	40	38	20
8	70	30	42	26
9	80	20	55	34
10	90	10

EFFECT OF ALKALI AND ALCOHOL

The concentrated sulfonated oils on the market usually contain a small amount of soap but a much greater quantity of free fatty acids. It was found that the completely neutralized oil is somewhat less soluble in mineral oils, but considerably less soluble in olive oil. This is shown, in Table V, by the amount of oleic acid necessary to clear the sulfonated-oil mixtures before and after neutralization. Alcohol (3) added to the neutralized oil reduces the amount of oleic acid by liquefying the soap, but an excess of alcohol has the opposite effect. With mineral oils, there is an advantage in completely neutralizing the sulfonated oil, provided the proper amount of alcohol is also added, but not so with raw olive oil, since the large excess of oleic acid necessary to clear the mixtures, even in the presence of alcohol, renders the oil non-emulsifying.

TABLE V. EFFECT OF ALKALI ON THE MISCIBILITY OF SULFONATED OLIVE AND RAW OLIVE OR MINERAL OIL

(Determined by amount of oleic acid to clear)

	OLEIC ACID TO CLEAR %
Equal parts acid sulfonated olive and mineral oil	0
Equal parts neutralized sulfonated olive and mineral oil	2
Equal parts acid sulfonated olive and raw olive oil	12
Equal parts neutralized sulfonated olive and raw olive oil	34

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Extraction of Slag and Oxide Inclusions in Iron or Steel

Electrolytic Method

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MANY methods of extraction other than electrolytic have been devised for the determination of non-metallics in iron and steel, but none have been satisfactory for all types of oxides. The outstanding method at the present time is the Dickenson method (2) which will extract silicon dioxide and aluminum oxide from "killed" steels with varying degrees of accuracy. However, this method will not give a quantitative extraction of inclusions which contain ferrous and manganous oxide from "rimming" steels (4). In fact, after a detailed study of extraction methods proposed to date and outlined by C. H. Herty, Jr., and others (4), and by Westcott, Eckert, and Einert (7), it is seen that none are satisfactory for use upon steel. A large sample must be used, as it is absolutely necessary, in a study of inclusions, to have enough non-metallics extracted for the determination of their physical and chemical properties. Also the extraction must be fairly rapid and must not require from 2 to 6 weeks as does the Dickenson method.

As regards previous work on electrolytic methods, nothing was found regarding the extraction of oxide impurities from steel. It has been shown that manganous oxide could not be extracted in an acid or ferrous sulfate solution (5).

In the steel industry a constant effort is being put forth to make a better product, and a cleaner steel is one of the desired achievements. However, before the cleanliness of steels produced by various means can be compared, a method must be found to determine the amount, the character, and the source of the oxide impurities. This paper gives a method for the extraction of these oxides from a solid block of steel, and it has been found to be better than any method published or suggested to date.

DESIGN OF CELL

The design of the cell has required much consideration and experiment, but the one finally chosen is simple of construction, costs only a few cents to make, and is easy to manipulate. It consists of two parts, an inner cell separated from the outer by means of a piece of filter paper. The steel or iron specimen is suspended in the inner cell by means of a platinum wire; the iron and metallic constituents go into solution, are ionized, and pass from the inner cell to the outer through the filter paper, and are plated out on the copper-screen cathode. The carbon, sulfur, and oxides remain in the inner cell and are collected in a filter paper cone which is removed for study of the residue.

AN ELECTROLYTIC method, rapid, simple in operation, and inexpensive, for the determination of oxides found in plain carbon steel and iron as inclusions, has been successfully developed. Magnesium iodide is used as the electrolyte and is found to be superior to any used heretofore.

The sulfides are not determined, but only the oxides of manganese, silicon, and iron. In the "killed" steels where the principal inclusion is manganous silicate, the recovery is practically 100 per cent; in the "rimmed" steels, slightly less.

The accuracy of the method has been determined through the use of slaggy material containing various percentages of ferrous, manganous, silicon, and aluminum oxides. This material was actually formed in the rimmed ingot of steel, and was collected for the study. It is believed that such material is a definite improvement over the use of synthetically prepared compounds, as it is the same physically and chemically as the inclusions dispersed throughout the steel itself.

The outer cell is a large-mouth reagent bottle of about 3 liter capacity, with a cork to fit. The inner cell is a smaller reagent bottle with the bottom cut off. The cork of the outer cell has a hole cut in it to fit the neck of the inner cell, and these are fastened together so as to support the inner cell. The cork fitting the smaller bottle has a hole punched in it for the platinum wire to pass through.

The cathode is made of the ordinary copper screen used in window screens. A piece is cut as long as the circumference and as wide as the straight sides of the large bottle. Two strips of screen are fastened as contacts to the screen itself. It is then rolled up and inserted into the bottle, where it unrolls and forms a cylinder. The contact strips are bent down on the outside of the bottle neck and fastened together with a third

band of wire screen. Figures 1 and 2 show the cell in detail.

PREPARATION OF ELECTROLYTE

The electrolyte used is magnesium iodide solution containing a small amount of free iodine. Magnesium was chosen because it should, and actually does, prevent the formation of ferrous hydroxide owing to magnesium hydroxide being less soluble. As the solution becomes slightly more alkaline due to evolution of hydrogen during electrolysis, magnesium hydroxide is precipitated. However, very little precipitation does occur, and the iron is plated out without being hydrolyzed. Magnesium iodide is a good conductor, and iron can be plated out at the rate of 1 gram per hour at 1 ampere and 4 volts.

To make 3 liters of solution, 120 grams of resublimed iodine are weighed into three 600-cc. beakers, and 400 cc. of distilled water added to each. Metallic magnesium is added gradually with stirring, until the iodine color disappears. The solution is filtered and 5 grams of iodine dissolved in it, and enough distilled water added to make the solution to 3 liters. It is then ready for use.

The same solution may be used repeatedly by filtering after each determination, and dissolving 5 grams of iodine in it.

PREPARATION OF STEEL SPECIMEN

The size of the specimen is controlled by the time desired to spend on the determination and the cleanliness of the steel. Ordinarily a 50-gram specimen is large enough. The portion to be decomposed is submerged in the solution, and the remainder is unaffected.

Any shape or size may be used. It must be filed clean of all oxides and cleansed of grease and oil. A platinum wire is wrapped around one end of the specimen and the contact protected by a piece of rubber sheeting or tubing held in place by rubber bands. It is also a good plan to coat the rubber and any part of the specimen not submerged with collodion to prevent corrosion and rust.

The weight of the sample actually used is found by weighing the piece before and after electrolysis, as there is always a little piece left, held by the contact above the solution.

ASSEMBLY OF CELL AND ELECTROLYSIS

When the cell is made, the electrolyte prepared, and the steel specimen fastened to the wire, the determination may be started. An ashless 11-cm. filter paper is folded as for use in a funnel and slipped into the inner cell so as to act as a receiver for the oxides. An 11-cm. hardened filter paper is fastened over the bottom of the inner cell by means of rubber bands.

The steel specimen is placed so as to touch the center of the filter-paper cone, and is supported by the wire passing through the hole in the cork of the bottle.

The electrolyte is poured into the large cell, the wire screen connected to the negative terminal of a 12-volt storage battery, and the inner cell placed in position. It gradually fills with the solution coming in through the filter paper. The current is regulated by means of a variable resistance in the circuit, and held at 1 ampere. A greater amperage may be used, but the temperature will become too high and the ferrous iodide will be decomposed. The best temperature for the operation should be below 25° C. As the sample becomes smaller, more voltage must be impressed to maintain 1 ampere. The cell will operate until the steel is decomposed to the surface of the solution.

TREATMENT OF RESIDUE AND ANALYSIS OF OXIDES

When the electrolysis is complete, the inner cell is removed, and the solution allowed to drain. The rubber bands are cut and the paper used to separate the two solutions removed. The filter-paper cone containing the oxides and carbon "skeleton" is placed in a weighing bottle. Two grams of iodine are added, the paper torn up with stirring, and the bottle filled with alcohol. The solution is allowed to stand, stoppered, with frequent stirrings, for at least 24 hours. This treatment will decompose small metallic particles which have fallen from the specimen. However, in high-carbon steels, it is practically impossible to remove all the steel because of the carbon coating of the particles. Several alcoholic treatments with iodine will remove all but a small amount, from 1 to 10 mg. of iron.

The residue is then filtered by suction on an ashless No. 589 "Blue Ribbon" paper, using a platinum cone. It is washed several times with small amounts of alcohol, and then with cold potassium iodide solution, until the washings are no longer the color of iodine. It is then washed with cold water,

about 200 cc. being sufficient. If the steel has had silicon added to it, 150 cc. of boiling hot 10 per cent potassium hydroxide are used as a wash, allowing it to filter by gravity. This will remove all silicic acid, and does not dissolve any manganous oxide. Rimmed steel does not receive this alkali wash. The residue is then washed free of alkali with boiling hot water. The residue and paper are dried, and the carbon burned out at a low red heat.

Although many methods may be used for the analysis of the oxides, the following is suggested: The ignited residue is placed in a platinum dish and dissolved in 10 per cent hydrochloric acid containing 15 cc. of 25 per cent sulfuric acid. As soon as the iron oxide goes into solution, the glassy particles of silicates and the white aluminum and other oxides may be seen. The solution is boiled down and the sulfuric acid fumed strongly to dehydrate any dissolved silica. This is cooled, the sulfates dissolved in a little hot water and a few drops of nitric acid, and the silica is filtered off. This is ignited and determined as silicon dioxide by volatilization with hydrofluoric acid.

The residue from the silica volatilization is fused with potassium bisulfate until it is decomposed. It is then leached out in the filtrate from the silica. This solution is made strongly ammoniacal, and the hydroxides are filtered off. The precipitate is dissolved in nitric acid, reprecipitated with ammonia, filtered, and washed with hot water. It is then dried, ignited, and weighed as iron oxide. In low-carbon steels, below 0.10 per cent, this is the iron from the ferrous oxide of the steel and is considered as such. In higher carbon steels, it is often contaminated with an appreciable amount of metallic particles and is calculated as metallic iron. The total silicon dioxide and manganous oxide found in the residue are corrected for the silicon and manganese coming from the metallic residue, as shown by the steel analysis. This is especially important in killed steels with 0.80 to 1.00 per cent carbon and high manganese and silicon contents.

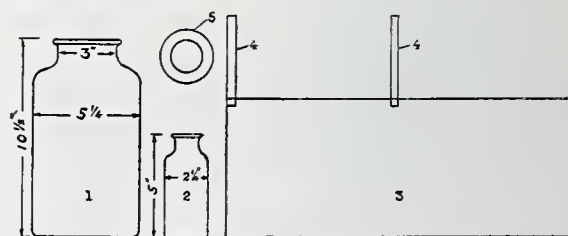


FIGURE 2. CELL PARTS UNASSEMBLED

The iron oxide contains a small amount of manganese tetroxide (Mn_2O_4) and aluminum oxide, and therefore it is fused with potassium bisulfate until it is all in solution, cooled, leached out, and added to the filtrate from the iron determination. This is then boiled down to 75 cc. and transferred to a 300-cc. Erlenmeyer flask.

To the solution in the flask, 30 cc. of acid mixture (1313 cc. of water, 625 cc. of concentrated nitric acid, 325 cc. of phosphoric acid, 250 cc. of sulfuric acid); 15 cc. of silver nitrate solution (16 grams in 2000 cc. of water); and 20 cc. of ammonium persulfate solution (600 grams in 2040 cc. of water) are added. This is brought to the boiling point and allowed to boil briskly for 1 minute, and is then cooled to 20° C. Cold water (75 cc.) is added and the manganese titrated with a standard arsenite solution (1 cc. = 0.0005 gram of manganese). This gives the total manganese, and after correcting for the trace due to metallic contamination, is calculated as manganous oxide. This method is as accurate as the bismuthate method and probably less open to error.

If the aluminum oxide is desired, the silver nitrate is removed as silver chloride, and the aluminum determined as aluminum phosphate after separating the iron from the aluminum with an excess of sodium hydroxide. The first

precipitation always contains a trace of iron and must be purified by at least one other separation. It is perhaps better to determine the aluminum oxide on a separate sample using the direct hydrochloric acid method for separation

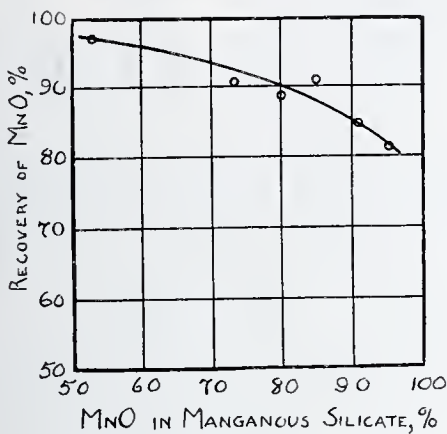


FIGURE 3. EFFECT OF ELECTROLYTIC EXTRACTION ON MnO

and determination as aluminum phosphate in ammonium acetate solution. However, it may be determined satisfactorily on the solution containing the manganese as given above.

ACCURACY OF DETERMINATION

The accuracy of the electrolytic extraction and recommended treatment of the oxides has been studied and found to give better results than any method used heretofore. It is known that all the manganese and ferrous sulfides are decomposed by the iodine to form free sulfur and the corresponding iodide. A wet oxidation and gravimetric determination of the sulfur in the electrolytic residue, calculated in terms of grams of steel electrolyzed, will give the ordinary sulfur determination on the steel drillings. There is no evidence of sulfidic sulfur. Also, the phosphides and the carbides are completely decomposed.

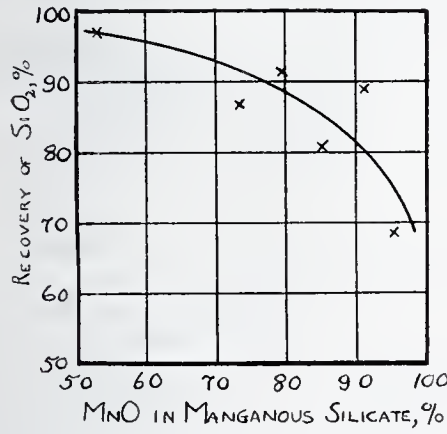


FIGURE 4. EFFECT OF ELECTROLYTIC EXTRACTION ON SiO2

In order to determine the accuracy of the extraction, oxides of varying composition of iron, manganese, silicon, and aluminum were placed in contact with the steel specimen for a period of 24 to 36 hours, during which the iron was electrolyzed at the rate of 1 gram per hour. These oxides had been ground to pass through a 100-mesh screen, and therefore offered a large surface to the action of the various solutions. After the extraction they were removed from the cell and treated with alcoholic iodine, then were filtered and washed with alcohol, potassium iodide solution, and cold water, then with hot water and 10 per cent solution of potassium hydroxide, and finally with hot water until all the alkali was removed. The

oxides were then analyzed to determine the effect of the treatment. The analyses are given in Table II.

These oxides were not the usual synthetic oxides prepared in the laboratory but were material taken from various rimmed ingots. They were the same as the inclusions dispersed throughout the steel, but which, during the rimming action, rose and were trapped in the upper portions of the ingot. These oxides are actually, chemically, and physically similar to the slags found in the steel as inclusions, and as such are much superior to the synthetic product for these experiments. Of course, the composition cannot be controlled, but it was found that in the six samples collected none were alike. The analyses of these slags are shown in Table I.

TABLE I. COMPOSITION OF SLAGS

CONSTITUENT	1	2	3	4	5	6
	%	%	%	%	%	%
SiO ₂	2.51	10.42	5.56	26.41	7.81	11.86
Al ₂ O ₃	2.96	5.56	1.67	29.66	5.36	4.57
MnO	49.78	41.40	57.20	29.93	44.98	32.51
Total Fe as FeO	43.21	39.88	35.38	8.36	38.47	37.18
Actual FeO	40.32	34.35	30.10	3.74	33.69	31.89
Fe ₂ O ₃	1.85	5.61	3.19	5.13	4.29	5.00
Fe	0.95	0.37	1.87	^a	0.78	0.68
CaO	0.61	0.74	0.15	2.70	0.80	10.10
MgO	0.70	0.88	0.07	2.90	1.45	2.66
P ₂ O ₅	0.021	0.014	0.092	^a	0.114	0.690
Total S	0.140	0.142	0.210	^a	0.260	0.170

^a Insufficient sample.

The effect of the electrolytic extraction and the subsequent treatment of the oxides has been compared with the effect of heating the oxides in a stream of pure, dry chlorine gas at a temperature of 450° to 500° F. (232° to 260° C.). The method of volatilization of iron in a current of pure chlorine is quite old, having been suggested by Fresenius in 1865 (3). This method of determining oxides in steel has been recently tested, revised, and recommended in spite of the fact that in the presence of phosphorus, sulfur, and carbon, there is an appreciable loss of oxides (1, 6). In this case, in the absence of the carbon and in the presence of the low percentage of the phosphorus and sulfur, the recovery is better than could be expected on a sample of steel. After the samples had been in the gas stream for a period of 4 hours, they were cooled and washed with cold water until the washings were free of chlorides. Then they were analyzed, and the analyses are shown in Table II.

TABLE II. EFFECT OF VARIOUS EXTRACTION METHODS ON SLAGS

SLAG SAMPLE	EXTRACTION METHOD	SiO ₂ %	Al ₂ O ₃ %	MnO %	TOTAL Fe AS FeO %
1	Fresenius	2.19	2.59	28.82	40.00
	Dickenson	0.05	1.67	0.97	1.36
	Electrolytic	1.71	2.79	40.48	44.83
2	Fresenius	10.09	5.33	29.93	39.49
	Dickenson	0.06	2.67	4.58	1.88
	Electrolytic	9.51	4.21	36.69	41.52
3	Fresenius	4.92	1.67	44.66	33.35
	Dickenson	0.08	1.10	0.45	0.23
	Electrolytic	4.94	1.55	48.44	34.54
4	Fresenius	25.73	30.12	24.71	8.04
	Dickenson	None	18.40	6.61	2.89
	Electrolytic	25.43	29.20	29.05	8.00
5	Fresenius	8.13	5.03	38.34	37.60
	Dickenson	None	3.61	1.45	2.50
	Electrolytic	6.10	4.97	40.82	38.84
6	Fresenius	11.91	4.74	29.29	36.02
	Dickenson	None	0.76	0.39	1.10
	Electrolytic	10.22	4.64	29.30	39.85

Also, the oxides were treated by the Dickenson method in the presence of a piece of steel. Although the method was originally introduced by J. E. Stead, it was developed in greater detail by Dickenson (2). This method of dissolving the iron in dilute nitric acid has been tried critically by Herty, Fitterer, and Eckel (4), and the procedure they recommend was used in this case. The results of this treatment of the oxides are also found in Table II.

From Table II it can be seen that the recovery of the manganous oxide is related to the percentage of the manganous oxide in the manganous silicate, $(\text{MnO})_x(\text{SiO}_2)_y$. This fact is very important as the oxides found in killed steels which have been deoxidized with ferromanganese and ferrosilicon

the electrolytic method is plotted against the per cent in the manganous silicate. From the curve it is quite apparent that the recovery of the manganous oxide in the manganous silicates found in killed steels is very high, close to 100 per cent, and over 80 per cent is recovered in the extraction of rimmed steels.

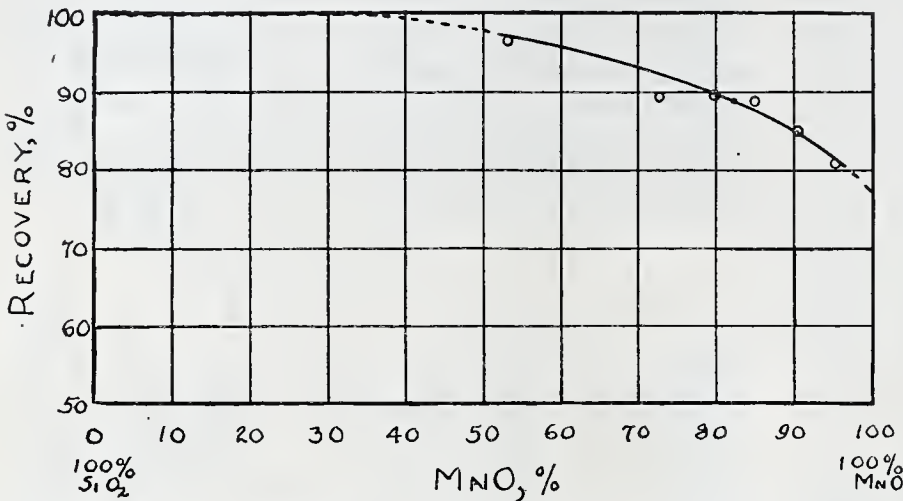


FIGURE 5. EFFECT OF ELECTROLYTIC EXTRACTION ON MANGANOUS SILICATES

are almost entirely manganous silicates with very little or no ferrous oxide. This relationship of recovery of manganous oxide to the percentage in the manganous silicate is shown in Table III.

TABLE III. COMPARISON OF MnO RECOVERED TO $\text{MnO}/(\text{MnO})_x(\text{SiO}_2)_y$ RATIO				
SLAG SAMPLE	$\frac{\text{MnO}}{\text{MnO} + \text{SiO}_2} \times 100$	MANGANOUS OXIDE RECOVERED		
		Fresenius method	Dickenson method	Electrolytic method
		%	%	%
1	95.20	57.89	1.95	81.32
2	79.89	72.29	11.06	88.62
3	91.14	78.08	0.79	84.69
4	53.12	82.56	22.09	97.05
5	85.21	85.24	3.22	90.75
6	73.27	90.10	1.20	90.10

From Table III it can be seen that the electrolytic extraction of the oxides is less harmful than either of the others. Although the chlorine gas method appears to be nearly as good it must be recalled that oxides of iron and manganese are appreciably affected and lost if carbon, phosphorus, and sulfur are present, as is the case in an actual extraction.

In Figure 3, the per cent of manganous oxide recovered by

TABLE IV. COMPARISON OF SiO_2 RECOVERED TO $\text{MnO}/(\text{MnO})_x(\text{SiO}_2)_y$ RATIO

SLAG SAMPLE	$\frac{\text{MnO}}{(\text{MnO}) + (\text{SiO}_2)}$	SiO_2 RECOVERED BY ELECTROLYTIC EXTRACTION
		%
1	95.20	68.13
2	79.89	91.27
3	91.14	88.85
4	53.12	96.29
5	85.21	78.11
6	73.27	86.17

The effect of the electrolytic extraction on the ferrous oxide cannot be determined, as the residue was contaminated with iron.

The alumina is recovered totally, or nearly so. In the analysis of the residue from rimmed steels, where the alumina is present the alkali treatment is omitted and the alumina completely recovered.

COMPARISON OF OXIDE DETERMINATIONS ON CARBON STEELS BY DIFFERENT METHODS

Several samples of high-carbon basic open-hearth steel, deoxidized with spiegeleisen and ferromanganese in the

TABLE V. COMPARISON OF OXIDE ANALYSIS ON DIFFERENT STEELS OBTAINED BY VARIOUS METHODS

SAMPLE	DESCRIPTION	STEEL ANALYSIS								OXIDE ANALYSIS		TOTAL OXYGEN	WEIGHT OF SAMPLE	EXTRACTION METHOD USED
		C	Mn	P	S	Si	Total manganous silicate	SiO ₂	MnO	SiO ₂	MnO			
		%	%	%	%	%	%	%	%	%	%	Grams		
1	Near top and outside of ingot	0.84	0.76	0.028	0.024	0.128	0.02971 0.00189 0.01990	0.02356 0.00162 0.01437	0.00615 0.00027 0.00553	79.30 85.71 72.21	20.70 14.29 27.79	0.0140 0.0009 0.0089	58.574 37.079 9.044	Electrolytic Dickenson Fresenius
2	Near top and center of ingot	0.72	0.62	0.025	0.024	0.198	0.0802 0.00286 0.0326	0.0509 0.00259 0.0274	0.0293 0.00027 0.0052	63.47 90.56 84.05	36.53 9.44 15.95	0.0337 0.0014 0.0158	27.506 27.049 6.924	Electrolytic Dickenson Fresenius
3a	Near top and outside of ingot	0.75	0.62	0.025	0.025	0.198	0.0092 0.00163 0.0180	0.0075 0.00141 0.0129	0.0017 0.00022 0.0051	81.52 86.50 71.67	18.48 13.50 28.33	0.0044 0.0008 0.0080	32.097 49.744 12.414	Electrolytic Dickenson Fresenius
3b	Near top and center of ingot	0.80	0.62	0.029	0.027	0.200	0.0200 0.00185 0.0296	0.0161 0.00168 0.0218	0.0039 0.00017 0.0078	80.50 90.81 73.31	19.50 9.19 26.69	0.0095 0.0009 0.0134	28.671 29.708 10.112	Electrolytic Dickenson Fresenius
4a	Near top and outside of ingot	0.55	1.42	0.027	0.028	0.182	0.0760 0.00212 0.0502	0.0300 0.00087 0.0382	0.0460 0.00125 0.0120	39.47 41.04 76.10	60.53 58.96 23.90	0.0264 0.0007 0.0231	24.667 46.078 10.731	Electrolytic Dickenson Fresenius
4b	Near top and center of ingot	0.62	1.42	0.033	0.029	0.186	0.0160 0.00210 0.0217	0.0134 0.00162 0.0154	0.0026 0.00048 0.0063	83.75 76.19 70.97	16.25 23.81 29.03	0.0077 0.0010 0.0096	29.814 37.071 9.740	Electrolytic Dickenson Fresenius
5	Near top and center of ingot	0.73	0.87	0.031	0.025	0.220	0.00595 0.00089 0.0206	0.00485 0.00077 0.0177	0.0011 0.00012 0.0029	81.51 86.51 85.92	18.49 13.49 14.08	0.0028 0.0004 0.0100	55.560 38.889 10.370	Electrolytic Dickenson Fresenius
6	Near top and outside of ingot	0.76	0.87	0.032	0.029	0.200	0.0160 0.00170 0.0219	0.0134 0.00160 0.0141	0.0026 0.00010 0.0078	83.75 94.12 64.38	16.25 5.88 35.62	0.0077 0.0009 0.0093	62.918 31.185 9.944	Electrolytic Dickenson Fresenius

TABLE VI. TYPES OF RESULTS OBTAINED BY ELECTROLYTIC METHOD ON RIMMED STEELS

SAMPLE	STEEL ANALYSIS				ELECTROLYTIC EXTRACTION					TOTAL O ₂ IN STEEL
	C	Mn	P	S	SiO ₂	MnO	Al ₂ O ₃	Al ₂ O ₃ ^a	FeO	
	%	%	%	%	%	%	%	%	%	%
1	0.04	0.35	0.039	0.019	0.00510	0.00150	0.00309		0.272	0.065
2	0.08	0.39	0.072	0.034	0.00324	0.00084	0.00289		0.227	0.054
3	0.03	0.02	0.004	0.024	0.00272	0.00024	0.02310		0.407	0.103
4	0.03	0.04	0.019	0.041	0.00265	0.00072	0.00620	0.0067	0.295	0.070
5	0.04	0.27	0.010	0.040	0.00315	0.00156	0.00650		0.173	0.044
6	0.06	0.27	0.012	0.041	0.00675	0.00087	0.00677		0.405	0.088

^a Determined by the direct hydrochloric acid method.

furnace, and with ferromanganese and ferrosilicon in the ladle, have been analyzed for manganous silicates by the electrolytic, Dickenson, and chlorine gas extractions. These samples were cut from adjacent positions and so should be nearly identical in regards to oxide content. The extractions were carried out in the same manner as has been outlined, and the results are shown in Table V. The total oxygen in the steel is calculated from the oxygen of the silicon dioxide and the manganous oxide on the assumption that the steel is completely deoxidized, and all the oxygen is combined in these oxides.

Table V shows the Dickenson method to be very destructive to the manganous silicates found in the killed steel. However, it is true that an analysis of the residue recovered by this method may give an indication of the relative amounts of manganous oxide and silicon dioxide in the silicates. The time required for the determination is prohibitive to routine analysis.

The chlorine gas extraction at the low temperature used gives apparently good results, but the fact that only 10 grams may be used in the extraction causes the oxide residue to be so small that very accurate results are difficult to obtain. Also, the small sample makes the analysis representative of a local condition. Another difficulty is that at this low temperature of volatilization the manganese is not volatilized but remains in the residue and must be washed out with the cold water.

Carbon has a power of absorption that makes this step difficult, and error may occur here as the actual manganous oxide is present in such small quantities.

The electrolytic extraction gives the best results, most nearly representative of the steel. A large sample is used and the oxides extracted are enough for an accurate analysis.

All the methods use clean and polished solid pieces of steel, eliminating any surface oxidation which may occur in any method using drillings or millings.

In Table VI are shown types of results obtained through electrolytic extraction on rimmed carbon steels.

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Improved Soxhlet Extraction Apparatus

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ALTHOUGH a large number of different devices are available for the continuous extraction of solids with volatile solvents, the familiar Soxhlet apparatus is still widely used because of its general adaptability. The various types of Soxhlet apparatus now in use have, however, certain manifest disadvantages. The use of cork stoppers is undesirable because of leakage and the presence of extractable matter (3). Ground-glass connections, although obviating the latter difficulty, do not entirely eliminate leakage and are distinctly fragile. In extraction apparatus such as the Wiley-Soxhlet of 1912 (2), the Underwriters Laboratory model of 1912 (1), the Bailey-Walker of 1914 (5), or the Pickel of 1919 (4), these disadvantages have been overcome, but in these types the solvent functions at or near its boiling point which is undesirable, as pointed out by Ford in 1912 (2), when working with non-homogeneous solvents. A further objection is the limited amount of sample that the extraction tube will contain.

Probably the most successful type of Soxhlet extractor now available is that employing a ground-glass joint between the condenser and extractor, and a mercury seal between the extractor and flask. In the apparatus described here the mercury seal is retained, but all other joints exposed to the

vapor of the boiling solvent are eliminated—a characteristic of the improved types of apparatus referred to above.

The modified apparatus is illustrated in Figure 1, which is practically self-explanatory. The body of the extractor is extended considerably above the vapor inlet, and condensation is effected by means of a separate condenser inserted into this upper portion, and is held in place by a wide flange on the top. The entire apparatus is constructed of Pyrex glass, which, together with the absence of fragile ground joints, makes a very rugged and serviceable outfit, well adapted to routine work.

It will be noted that the water inlet and outlet tubes of the condenser are practically vertical, instead of the usual bent-at-right-angles type. This arrangement was adopted for convenience in setting up a battery of extractors, such as illustrated in Figure 2, which shows a battery of six modified extractors heated by a water bath operated by a 330-watt immersion heater. A set-up of this kind is perfectly safe for use with the most volatile or inflammable solvents, and has been operated in these laboratories for some time with excellent results. Ether and carbon bisulfide extractions extending over a period of 3 to 4 days have been made without any

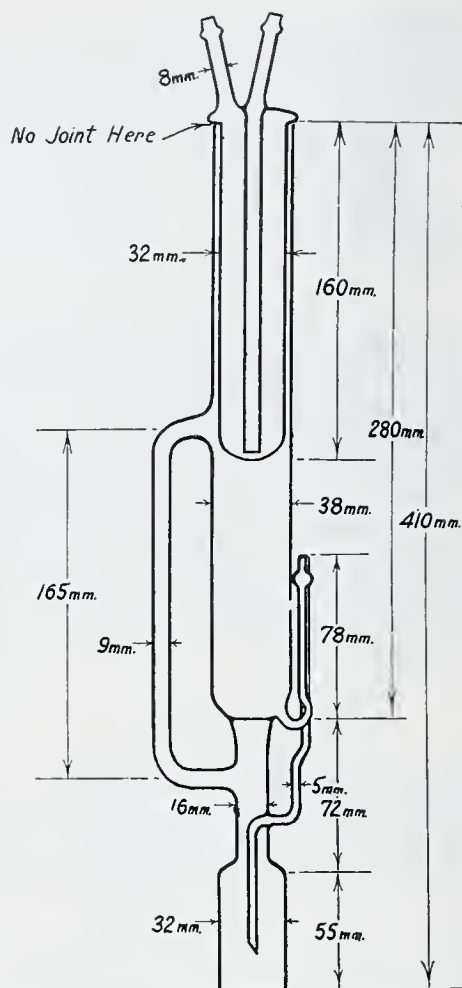


FIGURE 1. DIAGRAM OF APPARATUS

attention whatsoever and without any addition of solvent after the initial charge has been introduced.

The modified apparatus is no more difficult to operate than the conventional Soxhlet with attached condenser. A short loop of stiff wire is made across the water inlet and outlet tubes, and is used to suspend the condenser from a hook of brass rod, placed at such a height that the condenser freely clears the top of the extraction tube during the introduction or removal of sample or solvent. If the thimble containing the sample is plugged with extracted absorbent cotton, it may be removed by simply inverting the apparatus, for otherwise it is necessary to employ a pair of long dissecting forceps.

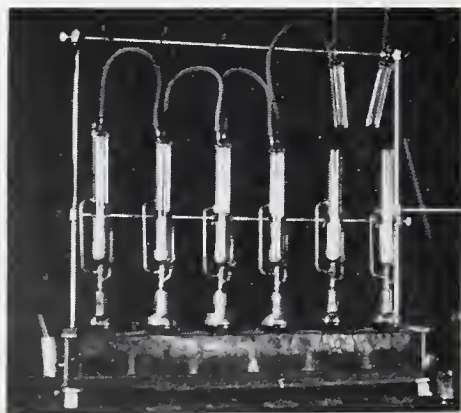


FIGURE 2. BATTERY OF MODIFIED EXTRACTORS

The dimensions given in Figure 1 correspond with those of the standard Soxhlet designed to take a 33 by 80 mm. thimble, but extractors of identical construction and of very large capacity have been made in this laboratory by the use of the largest Pyrex tubing available (60 mm. in diameter). These

extractors have proved of great value in large-scale extractions, enabling the entire operation to be performed within all-glass equipment, thus replacing metal apparatus and eliminating cork stoppers and rubber or ground-glass connections.

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Mechanical Shaking Device

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THE accompanying diagram shows the construction of an inexpensive shaking device which may easily be made in the laboratory. It was designed for use in the study of the corrosive action of milk on metals, and so made that the liquid flowed constantly over the immersed strips of metal.

The device consists of a metal water bath, 12 inches (30.5 cm.) in diameter by 20 inches (51 cm.) high. The remaining parts are of wood, painted to prevent warping. The drive shaft is connected to a metal eccentric, which is attached to the chuck of a friction drive stirrer. This permits convenient regulation of the rate of shaking, while the length of the stroke is controlled by the point of attachment of the drive shaft.

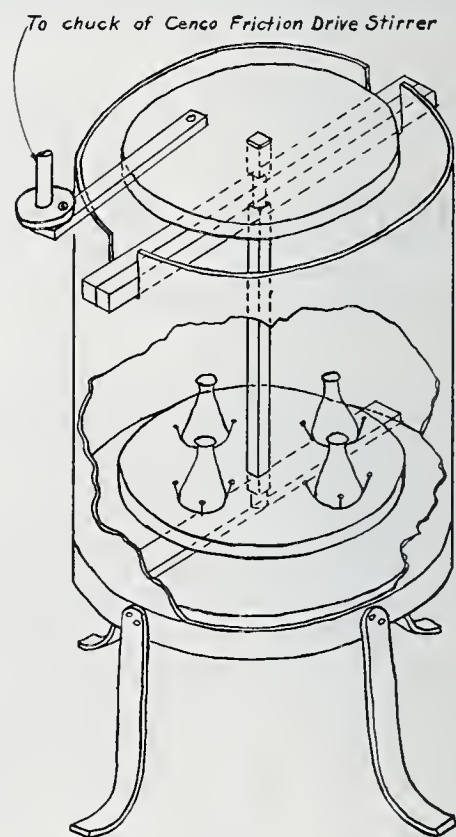


FIGURE 1. MECHANICAL SHAKING DEVICE

The apparatus described furnished a satisfactory shaking device at a low cost.

RECEIVED July 28, 1931.

Bi-Ortho-Anisidine as Internal Indicator in Bichromate Method for Iron

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RECENT research in volumetric analysis has revealed several useful inside indicators suitable for titrating iron with a standard solution of potassium bichromate. Diphenylamine and diphenylbenzidine, which were introduced by Knop (1) in 1924, have proved to be very satisfactory under most conditions. Occasional failures result, however, because, as Kolthoff and Sarver (2) have pointed out, these indicators are sometimes oxidized, not to the blue holoquinoid, but to a green meriquinoid which cannot be distinguished from the chromic chloride formed by the reduction of the standard solution of potassium bichromate. Moreover, even when a mixture of concentrated sulfuric acid and concentrated phosphoric acid is used to bind the ferric ions, many chemists have difficulty in detecting the color change from blue-green to blue.

In 1930 Szebellédy (3) overcame the latter objection by using ammonium fluoride to bind the ferric ions and *p*-phenetidine as the inside indicator. Under these conditions the iron solution retains a light yellow-green color until the first excess drop of bichromate solution produces a rich violet. The author (4) found in 1931 that *p*-anisidine may be used exactly like *p*-phenetidine, and that the oxidation product is equally brilliant in color. Unless these indicators have been freshly prepared, however, the violet oxidation product will appear too soon, and the results reported for iron will be too low.

For these reasons it seemed advisable to continue the search for oxidation indicators. Solutions of a number of aromatic amino derivatives were acidified with hydrochloric acid and treated with a slight excess of a dilute solution of potassium bichromate in order to observe any color changes that might appear. *p*-Phenylenediamine hydrochloride gave a green color which gradually changed to a rich purple, whereas *o*-phenylenediamine hydrochloride, *o*-anisidine, and bianisidine all gave a blood-red color. Only the latter substance, however, proved to be suitable for quantitative work.

PREPARATION OF MATERIALS

A 1 per cent solution of bianisidine in glacial acetic acid was prepared, and kept in a dark bottle. A quantity of Mohr's salt, ferrous ammonium sulfate, to be used as a standard was analyzed by weighing the iron as ferric oxide and by titration with a permanganate solution which had been standardized against sodium oxalate. The gravimetric and volumetric results agree closely.

The standard solution of potassium bichromate was made by dissolving 10.0005 grams of the dry, recrystallized salt and diluting to the mark with distilled water at 28° C. in a calibrated flask whose capacity at that temperature was found to be 1999.7 cc. The iron value of this solution was therefore

$$\frac{10.0005}{1999.7} \times \frac{0.05584}{0.04904} = 0.005695 \text{ gram per cc.}$$

Standardization of this solution against the ferrous ammonium sulfate yielded the same result—that is, 10 grams of potassium bichromate dissolved in water and diluted to 1 liter gave an iron value of 0.005695 gram per cc. Two other bichromate solutions similarly standardized and having iron values of

0.0055696 and 0.005694 gram per cc. were used in a few of the titrations.

BIANISIDINE AS INTERNAL INDICATOR

Four portions of the Mohr's salt were titrated by the following method: The solution obtained by dissolving the weighed sample in 30 cc. of 7 *N* hydrochloric acid was heated to the boiling point and carefully reduced with stannous chloride. After addition of one excess drop of stannous chloride, the iron solution was quickly diluted to 400 cc. with distilled water which had been cooled on ice. After adding 12 cc. of a mixture containing equal volumes of concentrated phosphoric acid and concentrated sulfuric acid, exactly 10 drops of the 1 per cent solution of bianisidine, and 30 cc. of a saturated solution of mercuric chloride, the iron solution was immediately titrated with the standard solution of potassium bichromate until the color passed through brownish green to red-brown. If the standard solution is added slowly toward the end, the color change is very distinct and the titrations can be duplicated very accurately. After standing a few minutes the titrated solutions acquire a blood-red color.

The results presented in Table I show that iron can be titrated accurately by this method. Although the indicator is not sharply reversible, iron solutions which have been over-titrated may be treated with a small measured volume of a standard ferrous solution and then correctly titrated with the standard solution of potassium bichromate.

TABLE I. BIANISIDINE AS INDICATOR IN TITRATION OF MOHR'S SALT

(After reduction with stannous chloride)				
	1	2	3	4
Mohr's salt, grams	1.5026	1.5046	1.5085	1.5024
Potassium bichromate, cc.	37.49	37.63	37.66	37.53
Iron value	0.005696			
Iron found, %	14.21	14.24	14.22	14.23
Mean, %	14.22			
Value from previous analysis	14.21			

TABLE II. BIANISIDINE AS INDICATOR IN TITRATION OF SIBLEY IRON ORE 27

(After reduction with stannous chloride)						
	1	2	3	4	5	6
Ore, gram	0.4012	0.4019	0.4003	0.4009	0.3999	0.4013
Potassium bichromate, cc.	48.64	48.80	48.61	48.64	48.46	48.72
Iron value	0.005695					
Iron found, %	69.04	69.15	69.16	69.09	69.01	69.14
Mean, %	69.10					
Bureau of Standards value, %	69.2					

As a further test of the usefulness of this indicator, six portions of the Sibley iron ore 27 provided by the Bureau of Standards were analyzed by the following method: Each weighed portion of the ore was treated with 30 cc. of 7 *N* hydrochloric acid and 5 cc. of stannous chloride solution and heated just below the boiling point for several hours until no brown residue remained. The solution was then filtered through ashless filter paper into a 600-cc. beaker. After washing with hot water, the filter was ignited in a porcelain crucible, the small amount of residue was carefully fused with potassium pyrosulfate, and the dissolved melt was added to the iron solution in the 600-cc. beaker. This was slightly oxidized with a few drops of a permanganate solution, care-

fully reduced with stannous chloride, and treated exactly like the samples of ferrous ammonium sulfate.

The results found for iron, as shown in Table II, average 69.10 per cent, whereas the value reported by the Bureau of Standards is 69.2 per cent. The results with bianisidine are therefore correct to within about 0.1 per cent.

TABLE III. PERMANENCE OF BIANISIDINE SOLUTION

(Titration of Mohr's salt after reduction with stannous chloride)

	1	2	3	4
Mohr's salt, grams	1.5041	1.5022	1.5021	1.5034
Potassium bichromate, cc.	37.49	37.49	37.48	37.54
Iron value	0.005694			
Iron found, %	14.20	14.21	14.21	14.22
Mean, %	14.21			
Value from previous analysis	14.21			

PERMANENCE OF INDICATOR

In order to test the effect of light on the indicator, four portions of the ferrous ammonium sulfate were titrated by the

above method, using a bianisidine solution that had been exposed to light in a north window for 11 days. The results given in Table III show that this treatment did not impair the usefulness of the bianisidine solution.

ACKNOWLEDGMENT

The author wishes to make grateful acknowledgment of the helpful suggestions received from F. B. Dains.

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Aqua Regia and Base Metals

Rate of Corrosion of Iron and Nickel by Aqua Regia as Function of Its Composition and Time of Mixture

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SINCE the eighth century, when aqua regia was first mentioned, according to Mellor (3), much experimental work has been carried out to determine the nature of the reactions which take place when it is prepared and used, and the ratios of the constituents which give the best results in dissolving metals. Recently Priwoznik (5), and Hoke and Moore (2) determined the best compositions for dissolving gold and platinum, respectively, as approximately 4 volumes of hydrochloric acid to 1 of nitric, for the concentrated acids. Schmitz (6) studied somewhat the corrosion of nickel and chromium steels by aqua regia, but gave practically no data on this subject. Moore (4) made several suggestions as to the cause of the activity of aqua regia. Briner (1) has examined the monovariant system of phases with the two components, nitric and hydrochloric acids (pure), and has shown that the reaction $\text{HNO}_3 + 3\text{HCl} \rightleftharpoons \text{NOCl} + \text{Cl}_2 + 2\text{H}_2\text{O}$ is reversible. In all of the literature covered no work with aqua regia of low hydrochloric acid content nor a systematic study of the dissolving of base metals by this acid mixture has been mentioned.

EXPERIMENTAL PROCEDURE

From some rough preliminary experiments it was found that aqua regia low in hydrochloric acid had decidedly more

THE BEST CONDITIONS for the rapid solution in aqua regia of base metals, as exemplified by iron and nickel, have been determined, using ordinary laboratory concentrated hydrochloric and nitric acids and controlling the temperature only roughly. For each ratio and time of mixing before introduction of the metallic sample, the time of immersion and loss in weight are recorded, the rate of corrosion being calculated and plotted. Its greatest value is obtained at a definite acid ratio and time after mixing, the former differing greatly from the 4 volumes of hydrochloric to 1 of nitric widely used for dissolving the noble metals. For nickel, 3 volumes of hydrochloric to 40 of nitric, and for iron as low-carbon steel, 7 of hydrochloric to 20 of nitric constituted the best mixtures with approximately 30 and 12 minutes' mixing, respectively. In both cases the maximum rate of corrosion obtained is about 16 times that obtained with a 4 to 1 mixture of hydrochloric and nitric acids used at the time of maximum corrosiveness.

action on nickel than had that of standard composition, 4 volumes of hydrochloric acid to 1 of nitric. It was also found that the activity of the aqua regia as measured by the rate of solution of the metal varied with the time during which the component acids had been mixed. This would be expected by one who has worked with aqua regia and observed the color changes which take place after mixing it.

Since results of practical use were desired for the chemist who must quickly dissolve samples of metals, standard pure concentrated laboratory acids were used, approximately 70 per cent nitric and 38 per cent hydrochloric acid. These acids were directly mixed from the bottle. The composition of the resulting aqua regia was expressed in terms of percentage of hydrochloric acid to total acid, the water not being considered in the calculations. It increased, of course, as the percentage of hydrochloric acid did. In practice, excess acid is invariably used, and therefore in these experiments this was done, and the rate of solution of the metal assumed approximately constant during each run. In every case the sum of the volumes of hydrochloric and nitric acids used was 50 cc. The acid to be present in larger volume was first measured into a 250-cc. beaker, and then, at a time that was recorded, the other acid was added with gentle stirring. The metal samples measured approxi-

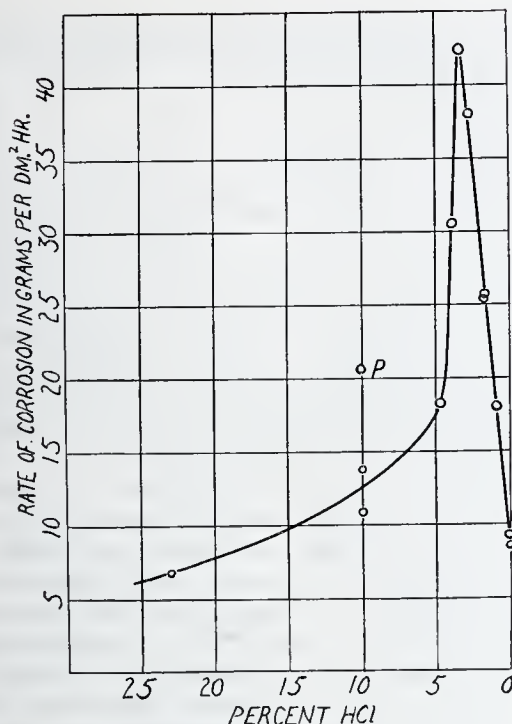


FIGURE 1. CORROSIVENESS ON NICKEL OF AQUA REGIA PREPARED 30 MINUTES

mately 50 by 20 by 4 mm. in size, and weighed about 30 grams each. Before each run the samples to be used were treated with a standard acid mixture for the same length of time, assumed long enough to give them similar surface structures. The samples were washed with water, then alcohol, and dried and weighed. At the proper time after mixing the acids, the metal sample was placed in the beaker with one end supported off the bottom by means of a short section of glass rod. This gave approximately equal convection conditions in the different runs. The action was allowed to continue long enough to dissolve about 20 to 50 mg., usually 30 to 300 seconds. Then the beaker was flooded with water, any surface powder washed off, and the sample

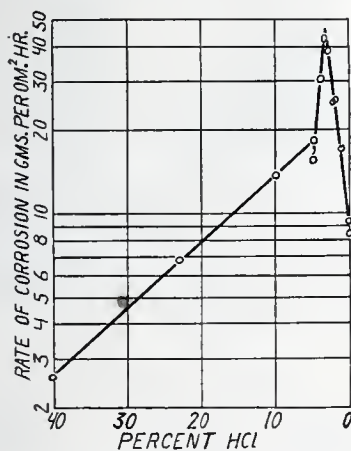


FIGURE 2. CORROSIVENESS ON LOG SCALE OF AQUA REGIA ON NICKEL

dried and weighed. The loss in weight was calculated to grams per square decimeter of apparent surface per hour. No attempt was made to determine the actual surface. The time of mixture of the acids was computed to the middle of the corrosion period, which was relatively much smaller and would permit this.

RESULTS FOR NICKEL

The nickel used was in the form of annealed sheets, and had the following analysis:

	%
Nickel	99.0
Copper	0.15
Iron	0.20
Cobalt	0.60

It was decided that 30 minutes would be a fair average for the time required by a chemist to prepare and weigh a sample to be dissolved, and therefore the aqua regia was used 30 minutes after being prepared, the immersion of the sample lasting 4 minutes more. From preliminary work it seemed probable that this time interval of 30 minutes would also correspond to near the time of maximum corrosiveness of the aqua regia for nickel. The temperature was kept between 15° and 20° C. by immersion of the beaker when necessary in colder water. Not much heat was generated. The data are plotted in Figure 1.

There is a very definite and sharp peak of high corrosion rate corresponding to about 3.3 per cent of hydrochloric acid, or 1 cc. of hydrochloric to 13 cc. of nitric acid. It was noticed that while the acid mixture was standing, streams

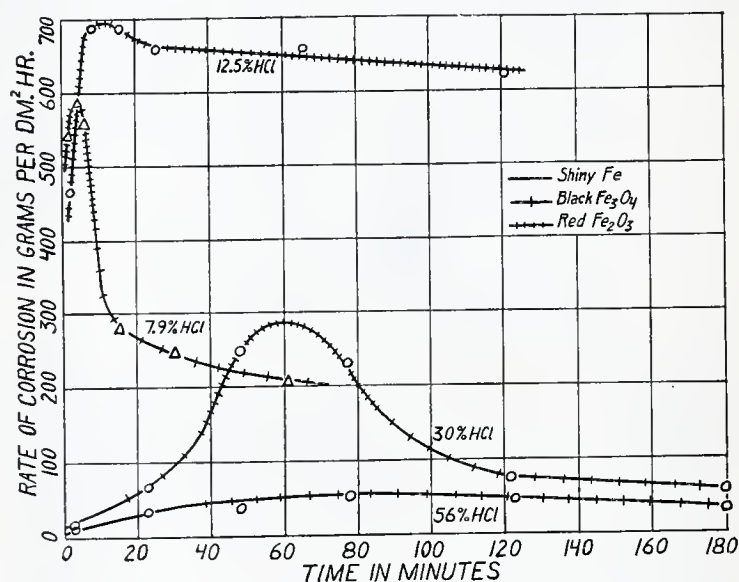


FIGURE 3. CORROSIVENESS OF AQUA REGIA ON LOW-CARBON STEEL

of small bubbles were liberated at a few points of the wetted surfaces, mainly the sharp edges of the section of glass rod supporting the end of the metal sample. This was ascribed to a catalytic action of a sharp edge, well known in heterogeneous reactions. The point corresponding to 10 per cent of hydrochloric acid was re-run with a newly cut section of glass rod instead of the former one, and a higher rate of corrosion was obtained, 13.7 grams per sq. dm. per hour instead of 10.7. Then the point was again determined, using eight of the glass sections of the same size, about 2 cm. long and 6 mm. in diameter. The rate of corrosion was found to have been raised further to 20.5, which is point P in Figure 1. Thus, sharp edges either increase the speed of only a heterogeneous reaction between the hydrochloric and nitric acids and possibly water, giving a mixture with the corrosiveness of one otherwise left standing longer, or else they increase the rate of some heterogeneous reaction over that of another, probably homogeneous. At the point for pure nitric acid (0.0 per cent hydrochloric) the action was not allowed to continue long enough to cause passivity of the nickel.

An interesting result was obtained by plotting the data on semi-log paper, as shown in Figure 2. It was seen that three practically straight lines constitute the graph. For each straight portion the relationship $dC/d(\%HCl) = kC$ holds, where C is the rate of corrosion and k a constant for

the line. Possibly over each of these straight sections a different reaction occurs between the aqua regia and the nickel, owing to changes in the reactions that occur between the hydrochloric and nitric acids.

RESULTS FOR IRON

It was decided that the effect of varying the time of mixture of the acids on the corrosiveness of the resulting aqua regia should be more carefully investigated. The iron samples were cut from a light structural steel member which had

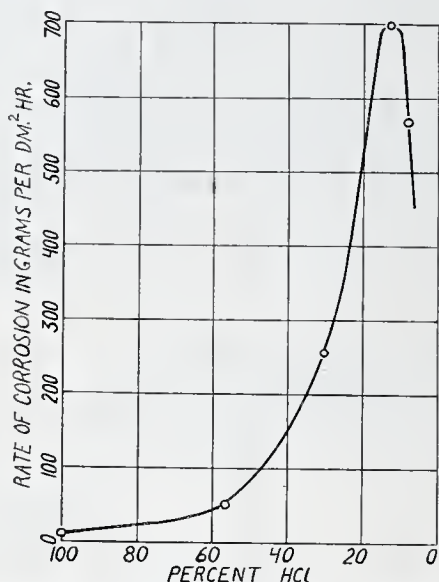


FIGURE 4. MAXIMUM CORROSIVENESS ON IRON vs. PER CENT HCl IN AQUA REGIA

been hot-rolled and contained 0.2 to 0.3 per cent of carbon. It was decided that actual conditions would be more closely approached if the temperature were not controlled. It also developed that owing to the more rapid action, it would have been much more difficult to control the temperature. The acids were mixed at room temperature and allowed to stand the required length of time, and the sample was inserted as before. The temperature then increased because of the action, and in several instances at points of high corrosion it reached the boiling point. Thus, if the temperature had been maintained low, the peaks of the rate of corrosion curves would have been lowered considerably, and the rest of the curves lowered somewhat also.

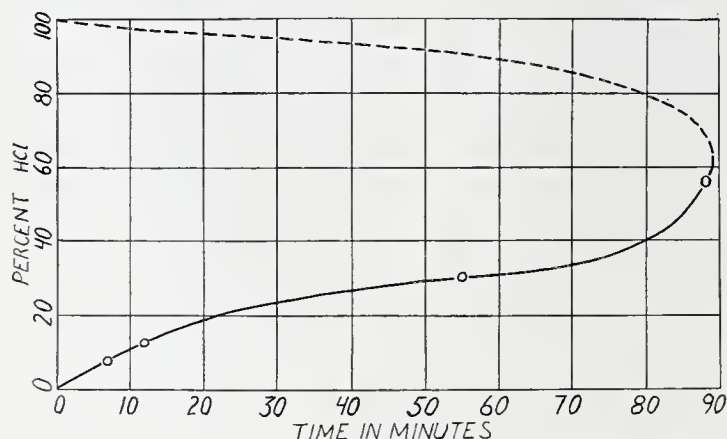


FIGURE 5. TIME OF MIXING FOR MAXIMUM CORROSIVENESS ON IRON vs. PER CENT HCl IN AQUA REGIA

Rates of corrosion were determined after varying times of mixing for aqua regia containing 56, 30, 12.5, and 7.9 per cent of hydrochloric acid. The results are plotted in Figure 3. It is seen that clearly defined peaks are obtained with the maximum rate of corrosion corresponding to a definite time of mixing the acids for a given aqua regia composition.

From these curves the maxima were taken and plotted against the corresponding percentages of hydrochloric acid in Figure 4, from which the maximum rate of corrosion for any given aqua regia composition can be obtained. From Figure 5 the requisite time of mixing the acids to give the maximum rate of corrosion can be obtained for a given aqua regia composition. It is seen that the highest rate of corrosion, 700 grams per sq. dm. per hour, corresponds to about 12 to 14 per cent of hydrochloric acid, and that it is obtained after 10 minutes' standing, although after about 5 minutes the corrosiveness has reached 600 and does not drop below this value for about 3 hours. This aqua regia is made from 7 cc. of hydrochloric acid and 20 cc. of nitric. If the samples had been left in long after boiling started, the rates of corrosion would be considerably increased.

These experiments took on added interest when it was observed that different products were formed by the action when differently constituted aqua regias were used. When the rate of corrosion was low, all of the iron dissolved passed to the form of ferric ions. However, at higher rates of solution, Fe_2O_3 or Fe_3O_4 was formed, either simultaneously with the ferric ions or as an intermediate step. At the highest rates only Fe_2O_3 was formed, besides ferric ion. These results are shown in Figure 3; no smaller ones have been seen mentioned anywhere in the literature.¹ These oxides were obtained on the surface of the samples after flooding at the end of the run. They were fine adherent powders, but easily wiped off, and usually did not cover the surface uniformly or entirely. The two oxides were never found together on the same sample. Their mass was always only a small fraction of the mass of the metal dissolved. Thus, an appreciable part of the action of aqua regia, if not a large part, at high rates of corrosion, forms oxides as an end product, probably owing to the nitric acid. The acids and ions present would cause some dissolving of the oxides, which must take place more slowly than their formation at these high corrosion rates.

Iron as a silicon iron was also studied for corrosion by aqua regia. The samples had the following composition:

	%
Silicon	14.5
Manganese	2.2
Carbon	1.0
Sulfur	0.1
Phosphorus, about	0.5
Iron, balance	81.7

The action on this metal was so slow as to be almost within the experimental error of the weighing for the time intervals of immersion that could be used. No water was added to the aqua regia; it is probable that more dilute acid would have more rapidly corroded the alloy.

ACKNOWLEDGMENT

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Determination of Traces of Carbon Monoxide in Ethylene

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THE importance of carbon monoxide when it occurs as an impurity in an anesthetic gas cannot be overestimated. Its affinity for the hemoglobin of the blood is variously reported to be from 210 to 300 times that of oxygen (9, 16, 31, 37). Since the carbon monoxide-hemoglobin compound that results is very stable, the oxygen-carrying power of the blood is seriously interfered with and tissue respiration impaired. It is obvious that the presence of even small traces of carbon monoxide in an anesthetic gas constitutes a serious danger. Early in the use of ethylene, cases were reported in which carbon monoxide poisoning occurred (35), but ethylene for anesthetic use which is free of carbon monoxide can now be obtained.

METHODS OF DETERMINING CARBON MONOXIDE

In detecting traces of carbon monoxide in ethylene, two obstacles are present that are not met with in determining the carbon monoxide content of other gas mixtures, such as the air of tunnels, garages, etc. These are (1) that very minute amounts of carbon monoxide must be detected, and (2) that in properties and behavior carbon monoxide and ethylene resemble each other very closely.

Though there are numerous satisfactory methods for the determination of the carbon monoxide content of air, some of which detect as little as 0.01 per cent by volume, they are not directly applicable to the problem of detecting smaller amounts of gas, especially in the presence of large amounts of the unsaturated hydrocarbon ethylene. The method of drawing air through a solution of iodine pentoxide and measuring the carbon monoxide content by the amount of iodine liberated cannot be used in the presence of ethylene, since unsaturated hydrocarbons give the same reaction (11, 14, 15, 18, 23, 24, 36).

Absorption of the carbon monoxide in solutions (either acid or ammoniacal) of cuprous chloride is unsatisfactory, since these also absorb ethylene, and some preparations absorb as much of one gas as of the other (7, 8, 41).

Tests depending upon the reduction of palladium chloride with the deposition of black metallic palladium are likewise not applicable in the presence of unsaturated hydrocarbons (3, 26).

Nickel forms nickel carbonyl, $\text{Ni}(\text{CO})_4$, with carbon monoxide at ordinary temperatures and, except for possible adsorption, there appears to be no reaction between nickel and ethylene. Nickel carbonyl is an unstable liquid, easily decomposed to give carbon monoxide. This reaction might be adapted to the detection of carbon monoxide in ethylene (29).

AS SHOWN IN the literature, there is great difficulty in determining traces of carbon monoxide in the presence of ethylene. The pyrotannic blood method is shown to be the most feasible for this purpose, and a recalibration of the "Pyrotannic Detector" color standard is given for use with carbon monoxide-ethylene mixtures.

A method of concentrating the carbon monoxide by fractional distillation at pressures less than atmospheric is described wherein the sensitivity of the pyrotannic blood method may be extended from 10 to 40 times. All of the carbon monoxide is shown to be obtained by this method in samples taken at the beginning of the first two distillations. Oxygenation of the reagent blood eliminates the necessity for running blanks.

Yellow oxide of mercury is quantitatively reduced by carbon monoxide at temperatures ranging from 0° to 100° C. (10, 30). No report was found indicating that ethylene reacts with this oxide, though it is well established that ethylene forms complex compounds with some of the mercury salts, notably mercuric cyanide, nitrate, and iodide (17, 40). Possibly the reduction of yellow oxide of mercury could be developed into a satisfactory test for carbon monoxide in the presence of ethylene.

Numerous procedures have been described for detecting the presence of carbon monoxide in air, based on the formation of carbon monoxide hemoglobin. Small animals such as mice,

canaries, and rabbits have been exposed to the air of mines, tunnels, etc., and by examination of their blood after exposure it has been possible to detect very minute traces of the gas (4, 6, 12). This could not very well be done in the presence of high concentrations of ethylene because of the effect of ethylene itself upon the animals.

In other hemoglobin methods that have been reported, the gas mixtures are brought into direct contact with solutions of blood or of hemoglobin (28, 32). The procedure developed by Sayers, Yant, and Jones is very widely used to detect carbon monoxide in air (34). The air is brought into contact with carbon monoxide-free blood for a period of time long enough to permit the formation of the carbon monoxide hemoglobin, and the blood is then treated with a mixture of solid pyrogallol and tannic acids to form a colored suspension. This is then matched with standards, a blood blank being run at the same time. This method will detect 0.005 per cent by volume of carbon monoxide in the air in regions of 0 to 0.05 per cent even by inexperienced observers. A possible objection to the adaptation of the method to the detection of carbon monoxide in ethylene is the formation of a compound of ethylene and hemoglobin, as has been described by Manchot (25). It will be shown, however, that by calibrating the color standards to known values of carbon monoxide in ethylene, satisfactory results can be obtained. In order to increase the sensitivity, methods of concentration were considered.

METHOD OF CONCENTRATING CARBON MONOXIDE

The removal of the ethylene before applying one of these tests, by absorption in fuming sulfuric acid or bromine water, might be applied to gas mixtures containing appreciable amounts of carbon monoxide, but this is not possible for amounts as low as one part or less in ten thousand. Even if the carbon monoxide were not lost in the manipulation, it would be lost by solution, since it is soluble to the extent of 2.33 cc. in 100 cc. of 95.6 per cent sulfuric acid, and is

¹ Holder of one of The Ohio Chemical and Manufacturing Company Graduate Fellowships for pure science research in anesthetic gases, 1927-29.

more soluble as the concentration of the acid increases (21). Furthermore, it reacts with bromine, especially in the light, to form carbonyl bromide. All non-aqueous liquids on which data were found dissolve more ethylene than carbon monoxide. Separation of the carbon monoxide by simple solution is therefore not feasible (2, 22, 27).

Both gases are adsorbed by numerous solid substances, including activated charcoal, dry hemoglobin, and certain preparations of nickel, copper, cobalt, iron, palladium, and platinum (13, 33, 38, 39). Carbon monoxide is much more extensively adsorbed than ethylene by charcoal and platinum black, and perhaps a concentration of this gas could be accomplished by this procedure.

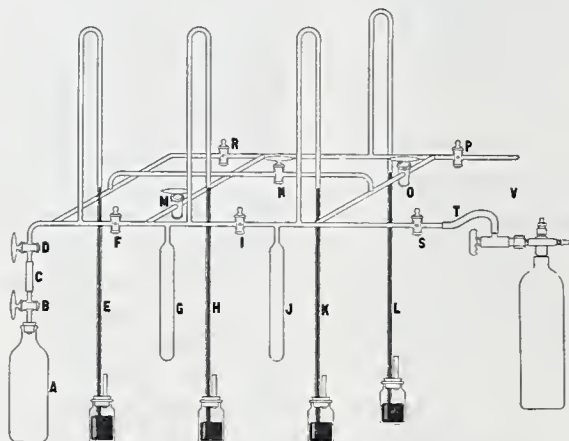


FIGURE 1. FRACTIONATING APPARATUS

The specific gravity, referred to air, of ethylene is 0.978, and of carbon monoxide, 0.967 (19). This excludes the possibility of separation or concentration of one component from mixtures of these two gases by diffusion.

The wide difference between the boiling points of the two gases suggests at once the separation by fractional distillation at low temperatures. Carbon monoxide boils at -192°C . and ethylene at -103.8°C . (20). This method has been made use of by Burrell and Robertson and others for the analytical separation of mixtures of hydrocarbon gases (5), and is the method adapted by the writers to the present problem of concentrating and separating carbon monoxide from mixtures with ethylene.

EXPERIMENTAL PROCEDURE

After consideration of the data presented above on the chemical behavior and physical properties of ethylene and carbon monoxide, it was decided that the method of approach to the problem of determining traces of the latter gas in preponderating volumes of the former should be to concentrate the carbon monoxide by fractional distillation, and then determine it by the pyrotannic blood method. The preliminary concentration should serve to extend the sensitivity of the test.

Previous work (unpublished) had demonstrated that separation of carbon monoxide from ethylene could not be effected under pressure; there appears to be some solubility of carbon monoxide in liquid ethylene which obviously, according to Henry's law, is increased with increased pressure. It is therefore impossible to fractionate off the carbon monoxide from a mixture in a high-pressure cylinder by chilling the cylinder below the critical point of ethylene (9.7°C). The

fractionations here described were conducted at atmospheric pressures.

A small steel gas cylinder (size "D") (1) was evacuated and filled to atmospheric pressure with carbon monoxide prepared from oxalic and sulfuric acids, and then with ethylene until the concentration of carbon monoxide was 0.01 per cent.

The fractionation apparatus of the intermittent type was constructed, as shown in Figure 1, entirely of glass, the parts being fused together with a hand torch. The only rubber connections were at *T* and *C*, where the cylinder and the sample bottle were connected to the apparatus. These connections were as short as possible, and were made of heavy pressure tubing; they held a vacuum satisfactorily. *J* and *G* were the bulbs in which the gas was condensed by bringing liquid air in a Dewar flask up around them. *K* and *H* were mercury safety manometers to indicate the pressure in *J* and *G*, respectively. *A* was a sample bottle of 300 cc. capacity, and *E* a safety manometer to indicate the pressure of the sample. *L* was a manometer for testing the efficiency of the pump.

The entire apparatus was evacuated by a rotary oil vacuum pump connected at *P*. The cylinder was then put in place and heated by surrounding it with water well above the critical temperature of ethylene. All stopcocks were closed, separating the fractionating bulbs and the sample bottle from one another. Liquid air was brought up around *J*, the cylinder valve, valve *V*, and stopcock *S* were opened, and ethylene condensed as a solid in the bulb. Since the gas in the cylinder was entirely in the gaseous phase, this was a representative sample of the contents of the cylinder. When 25 cc. of liquid ethylene had been condensed, the valves and stopcock were closed, and the ethylene in the bulb allowed to liquefy. When the liquid began to boil, the stopcocks *N*, *D*, and *B* were opened and a sample of gas collected in the sample bottle. When the pressure had reached atmospheric, as shown by the manometers *K* and *E*, stopcocks *B* and *D* were closed, and liquid air brought up around bulb *J* momentarily to prevent the pressure from increasing above atmospheric. The sample bottle was disconnected and a second one put

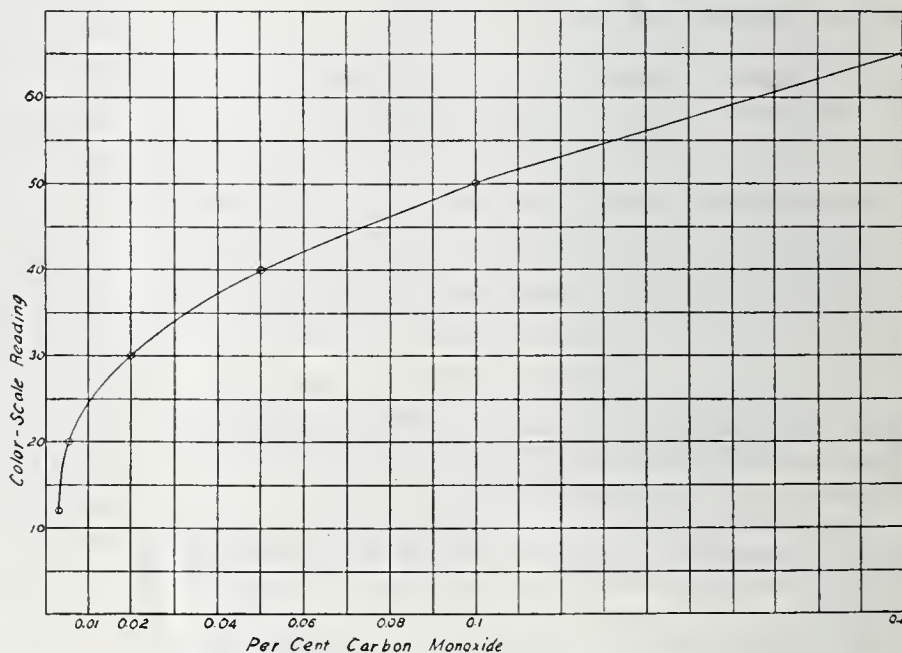


FIGURE 2. RECALIBRATED VALUES OF COLOR STANDARDS

in place and evacuated with the pump. The ethylene was allowed to boil and a second sample collected in the same way as the first. Stopcocks *B*, *D*, and *N* were then closed and stopcock *I* opened and, by bringing liquid air up around bulb *G*, the ethylene was distilled over into *G*. About midway of

the distillation the process was interrupted to collect a third sample. A fourth sample was taken at the end of the distillation.

All of the ethylene except that taken in samples 1, 2, 3, and 4, was now in bulb *G*. It was allowed to liquefy and, when boiling began, two consecutive samples, 5 and 6, were taken. The gas was then distilled back into bulb *J* by surrounding it with liquid air. Midway of the distillation, sample 7 was taken.

A third distillation was then made, condensing the ethylene again in bulb *G*. Sample 8 was taken at the start of this distillation, sample 9 midway, and sample 10 at the end. The remaining ethylene was discarded through a gas meter.

The gas samples were then analyzed by the pyrotannic blood method, the procedure being as follows:

A 1 to 20 dilution in water was made of blood from (animal) subjects that had not been exposed to carbon monoxide. Two cubic centimeters of this were run into the sample bottle containing the gas, which was re-corked immediately. The bottle was held in a horizontal position and rotated for 15 minutes, using a rotating machine. The blood was then poured into a small glass tube, 8 by 40 mm., and an equal amount of the diluted blood was placed in a similar tube to serve as a blood blank. Then 0.04 gram of 1 to 1 solid mixture of pyrogallol and tannic acids was added to each tube to develop the color and to form the colored suspensions. All of the procedure up to this point was conducted in a dimly lighted place. At the end of 15 minutes the tubes were compared with color standards by holding them against a dull black background, using reflected light. Sunlight or artificial light is not satisfactory. The tests should not be run where there is any likelihood of carbon monoxide being present in the atmosphere.

The color standards used were the "Pyrotannic Detector" set put out by the Mines Safety Appliance Co. of Pittsburgh, which had been recalibrated to ethylene-carbon monoxide mixtures. For this purpose accurate synthetic mixtures with 0.003, 0.005, 0.02, 0.05, 0.1, and 0.2 per cent carbon monoxide were made by first making accurate 5.0 per cent mixtures and diluting with pure ethylene in accurate mercury gas burets to these concentrations.

Table I gives briefly the recalibration, the readings being the averages of three sets of determinations, each observation made by four observers.

TABLE I. RECALIBRATION OF COLOR STANDARDS

CARBON MONOXIDE IN ETHYLENE	COLOR-SCALE READING
%	
0.5	80
0.4	75
0.3	70
0.2	65
0.1	50
0.05	40
0.02	30
0.005	20
0.003	12
0.001	0
0.0005	0
Blood blank	0

This shows the color scale not to be sensitive below a reading of 12, which represents 0.003 per cent by volume of carbon monoxide in ethylene. The curve for these values is given in Figure 2.

RESULTS

The results obtained by the analyses of the samples of gas from the fractionation of the carbon monoxide-ethylene mixture are shown in Table II.

The results in Table II show that all of the carbon monoxide present in the ethylene was obtained in the samples taken at the beginning of the first two distillations. Calculating the ethylene content of the three samples, 1, 2, and 5, on the basis of 300 cc. capacity for the sample bottles, the carbon monoxide content of the 10,100-cc. specimen amounted to

1.008 cc., or 0.010 per cent by volume. This is close to the lower limit of sensitivity of the test if determined directly, yet, as shown by the results given above, concentration by two fractionations made it quantitatively determinable. This fractional distillation was repeated a number of times with the same results.

To demonstrate further the value of the preliminary concentration of the carbon monoxide, and to confirm the results given above, a few results obtained by using specimens of crude ethylene are given in Table III showing how all the carbon monoxide is concentrated in the first fractions.

TABLE II. ANALYSES OF SAMPLES OF GAS FROM FRACTIONATION

SAMPLE	COLOR-SCALE READING	CARBON MONOXIDE IN SAMPLE Cc.
1. First, taken at beginning of 1st distillation	70	0.23 × 300 = 0.69
2. Second, taken at beginning of 1st distillation	45	0.074 × 300 = 0.222
3. Taken at mid-point of 1st distillation	2	None
4. Taken at end of 1st distillation	2	None
5. First, taken at beginning of 2nd distillation	35	0.032 × 300 = 0.096
6. Second, taken at beginning of 2nd distillation	5	None
7. Taken at mid-point of 2nd distillation	2	None
8. Taken at beginning of 3rd distillation	2	None
9. Taken at mid-point of 3rd distillation	2	None
10. Taken at end of 3rd distillation	2	None
Blood blank (correction insignificant)	2	
		Total 1.008

TABLE III. RESULTS WITH CRUDE ETHYLENE

CRUDE ETHYLENE SPECIMEN		COLOR-SCALE READING	CARBON MONOXIDE IN SAMPLE %	EQUIV. IN ORIGINAL %
SPECIMEN NO. 1				
1st dis- tillation	{ Sample 1, at beginning	25	0.011 corr. ≈ 0.00024	
	{ Sample 2, at beginning	10	to 0.010 Less than 0.003	
2nd dis- tillation	{ Sample 1, at beginning	Less than 5	None	
	{ Sample 2, at beginning	Less than 5	None	
SPECIMEN NO. 2				
1st dis- tillation	{ Sample 1, at beginning	30	0.020 corr. ≈ 0.00044	
	{ Sample 2, at beginning	10	to 0.018 None	
2nd dis- tillation	{ Sample 1, at beginning	Less than 10	None	
	{ Sample 2, at beginning	10	None	
SPECIMEN NO. 3				
1st dis- tillation	{ Sample 1, at beginning	38	0.042 corr. ≈ 0.00088	
	{ Sample 2, at beginning	15	to 0.038 None	
2nd dis- tillation	{ Sample 1, at beginning	10	None	
	{ Sample 2, at beginning	10	None	
Blood blank		15	None	

The quantitative application may be shown by calculating the carbon monoxide content of specimen No. 1 from the data given in this table. All of the carbon monoxide was obtained in the first sample of the first distillation, and amounted to 0.011 volume per cent, but the blood blank color-scale reading of 5 was equivalent to 0.001 per cent, leaving a real value of 0.010 per cent or 0.030 cc. of carbon monoxide in the 300-cc. sample. This is equal to 0.00024 per cent of the carbon monoxide in the 12,600 cc. of gas taken from the cylinder and is considerably below the sensitivity limit of the direct test. Without the preliminary fractionation it could not have been determined.

Charles H. Wardell, chief chemist of the Ohio Chemical and Manufacturing Company, in using this method for 3 years in controlling the purity of anesthetic ethylene, has found that, by oxygenating the blood before use by bubbling through it pure oxygen to a constant bright color, the blood blank becomes zero, thus simplifying the calculations greatly. It has been found also that oxygenated blood will keep in excellent condition in an electric refrigerator for over a week

if in a tightly stoppered bottle, whereas the untreated blood rapidly deteriorates.

To calculate the extent to which the sensitivity of the test is increased by this means, it is merely necessary to determine the ratio between the amount of gas taken from the cylinder and the amount taken as samples for the pyrotannic blood determination. If three samples are allowed, which, as has been shown, is a safe margin for obtaining all of the carbon monoxide, the ratio is 12,600 to 900 (3×300), or 1 to 14. As a matter of fact, however, all of the carbon monoxide is obtained in the first two samples taken, so that the ratio is really 1 to 20. Concentration by fractionation readily increases the sensitivity of the modified oxy-hemoglobin test 20 times. Obviously, by increasing the amount of the sample the sensitivity can be correspondingly increased.

ACKNOWLEDGMENT

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Germanic Sulfide

Quantitative Conversion of Sulfide to Dioxide by Hydrolysis

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GERMANIC sulfide is usually converted to dioxide by repeated treatment with nitric acid followed by evaporation and ignition to expel sulfuric acid from the residual oxide. It is known that this reaction is quite violent and that if the acid is diluted to cut down the violence of the oxidation, much free sulfur separates which is difficult to remove by subsequent treatment with excess of the oxidant. Small amounts of sulfide ordinarily dealt with in the quantitative determination of germanium may be converted to oxide in this way, but even here results are likely to be low unless extraordinary care is taken to prevent mechanical loss. The first decided improvement in the determination of oxide from the sulfide was described by Johnson and Dennis (1). These investigators dissolve the precipitated sulfide in ammonium hydroxide, oxidize with hydrogen peroxide, evaporate, and ignite to oxide.

GERMANIC SULFIDE can be conveniently transposed to dioxide by simple hydrolysis, the decomposition effected by injecting a current of steam into the water suspension of the sulfide. Hydrolytic decomposition of the sulfide in large masses is of special advantage because all processes involving oxidation of the sulfide are attended with violent reaction and accompanying errors.

Germanium can be quantitatively determined by hydrolyzing the sulfide directly to oxide, when it is weighed. Elimination of the sulfur as hydrogen sulfide avoids sources of error common to methods involving oxidation of the sulfide.

The present paper describes a new method of converting large or small amounts of germanic sulfide to germanic oxide by simple hydrolysis in which all of the sulfur is removed as hydrogen sulfide. The authors claim that the hydrolytic decomposition of the sulfide may be advantageously used both for an accurate determination of germanium and for the rapid conversion of large masses of the bulky sulfide to oxide in the preparation of pure germanium compounds.

EXPERIMENTAL PROCEDURE

A quantity of germanic sulfide was precipitated from a 6 N hydrochloric acid solution of the dioxide. (Arsenic-free material was used throughout.) The precipitation was carried out with hydrogen sulfide under pressure in a closed system to exclude air. The bulky white sulfide was rapidly filtered on Büchner funnels and washed with dilute hydro-

chloric acid saturated with hydrogen sulfide, then with alcohol saturated with the same gas, and finally with dry ether. The sulfide was quickly placed *in vacuo* to remove ether, remaining small amounts of moisture, and free hydrogen sulfide.

The product was kept in a well-stoppered weighing bottle from which samples were taken for most of the following experiments.

EXPERIMENT 1. A portion of this sulfide weighing 20.670 grams was placed in a liter flask with about 900 cc. of freshly distilled water. The flask was immersed in an oil bath and a slow current of carbon dioxide was passed through the suspended sulfide. The escaping gas was conducted through a series of wash bottles containing, in all, more than enough copper sulfate solution to absorb all of the hydrogen sulfide split off by hydrolysis, assuming the reaction to reach completion. Appreciable reaction began in the cold as evidenced by the separation of copper sulfide in the first several wash bottles. The temperature was slowly raised to the boiling point and a steadily increasing rate of decomposition was observed with the rise. At the boiling point the decomposition was quite rapid, and after about 3 hours no trace of hydrogen sulfide could be detected in the escaping gas. The flask was disconnected, and when the volume had been reduced by evaporation to about one-third of the original, its contents were filtered through an alundum cone to separate the undissolved micro-crystalline oxide from the saturated solution above it. It was observed that the original bulky mass of sulfide had become dense and finely crystalline as hydrolysis took place and, unlike the suspended sulfide, rapidly settled to the bottom of the flask as soon as the gas current was discontinued. Under the microscope the product of hydrolysis was distinctly crystalline, and in this respect was unlike the oxide formed by hydrolysis of the tetrachloride, as the crystalline nature of the latter can only be observed by x-ray spectral examination. The deposited oxide and the filtrate were separately analyzed for sulfur content to determine the extent of hydrolysis undergone by the original sulfide. This was accomplished by treating each with an excess of nitric acid followed by evaporation on a water bath and retreatment with fuming nitric acid to make sure of complete oxidation of any free sulfur or thio compound to sulfuric acid. After extraction with water, the sulfuric acid was determined in the usual way as barium sulfate. The barium sulfate from the filtrate weighed 0.0010 gram, whereas that from the undissolved oxide amounted to 0.0051 gram. The sum of these represents a total sulfur content of 0.0021 gram, which is only 0.02 per cent of the sulfur originally present in the sample of sulfide.

It is thus evident that it is possible to convert the sulfide to oxide completely by a reaction that does not involve oxidation, and that all, or practically all, of the sulfur can be expelled as hydrogen sulfide if air is excluded from the system.

EXPERIMENT 2. A mass of germanic sulfide weighing 75.0 grams was suspended in a 3-liter flask with about 1500 cc. of air-free water, and after expelling the air by carbon dioxide, a rapid current of steam was injected. Condensation of steam in the flask was prevented by immersing the container in an oil bath heated to 110° to 120° C. Large masses of the sulfide showed a tendency to foam during the first part of the reaction but this was successfully prevented by leading a second steam current into the flask through a small tube terminating above the surface of the boiling liquid. The main current of steam was introduced through a tube of larger bore which passes under the liquid nearly to the bottom of the flask. Analysis of the product of hydrolysis carried out as in experiment 1 gave a total sulfur content of 0.00146 gram, or 0.004 per cent of the sulfur present in the original sulfide.

Further experiments with still larger amounts of sulfide were made. In one case 300 grams of sulfide were converted to

oxide in about 2.5 hours by rapid steam injection. The residual mass of micro-crystalline dioxide so produced was then directly converted to tetrachloride in the same vessel by detaching the steam tube and replacing it with an inlet tube for hydrochloric acid gas and a condenser for the volatile tetrachloride which was caught in a chilled receiver. In dealing with some 300 grams of sulfide, the equivalent of 230 grams of oxide, it was convenient to use a 5-liter round-bottom flask containing 2 to 2.5 liters of water to effect the initial hydrolysis of the sulfide. The water remaining after hydrolytic decomposition could then be further reduced in volume or completely evaporated before introducing hydrochloric acid in sufficient excess to effect the distillation of the chloride from the same flask.

TABLE I. QUANTITATIVE CONVERSION OF GERMANIC SULFIDE TO DIOXIDE BY HYDROLYSIS

SAMPLE	GeO ₂ TAKEN Gram	GeO ₂ FOUND Gram	ERROR Gram
1	0.2519	0.2519	0.0000
2	0.1269	0.1260	-0.0009
3	0.0132	0.0129	-0.0003
4	0.0053	0.0058	+0.0005
5	0.0266	0.0259	-0.0007
6	0.0053	0.0057	+0.0004
7	0.0133	0.0137	+0.0004
8	0.0160	0.0163	+0.0003
9	0.2519	0.2519	0.0000
10	0.2519	0.2521	+0.0002
11 ^a	0.2519	0.2520	+0.0001
12 ^a	0.1259	0.1258	-0.0001
13 ^a	0.0050	0.0048	-0.0002

^a Sulfide precipitates hydrolyzed in weighed clear quartz beakers so that after removal of filter crucible, solution could be directly evaporated to dryness, ignited, and weighed in same vessel. This cancels errors arising from dissolved constituents of glass and avoids transference of partly evaporated solution to another vessel.

HYDROLYSIS APPLIED TO QUANTITATIVE DETERMINATION

Definite quantities of germanic oxide were obtained from several standardized solutions of pure germanic dioxide containing, respectively, 5.0380 and 0.5038 grams of oxide per liter. All flasks, pipets, and burets were carefully calibrated at 22° to 25° C.

The exact concentrations of the germanic oxide solutions used were determined by evaporating 50-cc. samples to dryness in weighed quartz beakers, and igniting the residue to anhydrous oxide at 900° C.

Various amounts of dioxide, as shown in Table I, were taken by pipet or buret into 0.25-liter Erlenmeyer flasks and all samples brought to approximately 50-cc. volumes by addition of water. Each sample was treated with enough concentrated sulfuric acid to give about 6 N free acid (7 to 8 cc. for each 50 cc. volume). Germanic sulfide was precipitated by attaching the flask or series of flasks to a hydrogen sulfide generator delivering the gas under pressure of about 2 feet (60.9 cm.) of water. Air was rapidly removed from the system by a brisk current of gas, and complete precipitation effected by allowing the hydrogen sulfide to remain in the closed system under pressure for at least 12 hours before filtering. The precipitated sulfide was removed by filtration through porous-bottom porcelain crucibles (15 cc. capacity), with coarse-grade filters purposely selected to make filtration as rapid as possible. The precipitate was washed with a little 1 N sulfuric acid saturated with hydrogen sulfide and sucked down as dry as possible on the crucible bottom. The crucible was then dropped into a beaker containing sufficient boiling water to immerse it completely, and active boiling was continued in the covered beaker until the hydrolyzed sulfide had completely entered solution. The small crucible was then removed and rinsed with a jet from the wash bottle. The solution was reduced by further evaporation to somewhat less than 40 cc. and then transferred to a weighed porcelain crucible in which evaporation to dryness was effected.

The dry or nearly dry residue was in each case treated with a few drops of nitric acid, although in no case could any noticeable action be observed. The treatment with acid was made, however, in order to oxidize any traces of free sulfur which may have formed by accidental oxidation of escaping hydrogen sulfide. Noticeable amounts of sulfur form only if the beaker containing the suspended sulfide is allowed to remain un-

covered during the initial hydrolysis or if the water is not kept actively boiling to exclude air while hydrogen sulfide is escaping. The residual dioxide was ignited at 900° C., as usual.

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A Vapor-Pressure Nomograph

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IN THE course of another investigation, the writers found it necessary to calculate many vapor pressures from data given in the International Critical Tables. Since much of these data are given in the form $\log p_{mm} = -(0.05223 A/T) + B$, where A and B are constants for the material under investigation, T the absolute temperature, and p_{mm} the vapor pressure in millimeters, certain mathematical and mechanical difficulties make calculation by ordinary methods difficult, particularly since a slide rule cannot be used directly. In order to simplify and speed up these calculations, the accompanying nomograph has been designed.

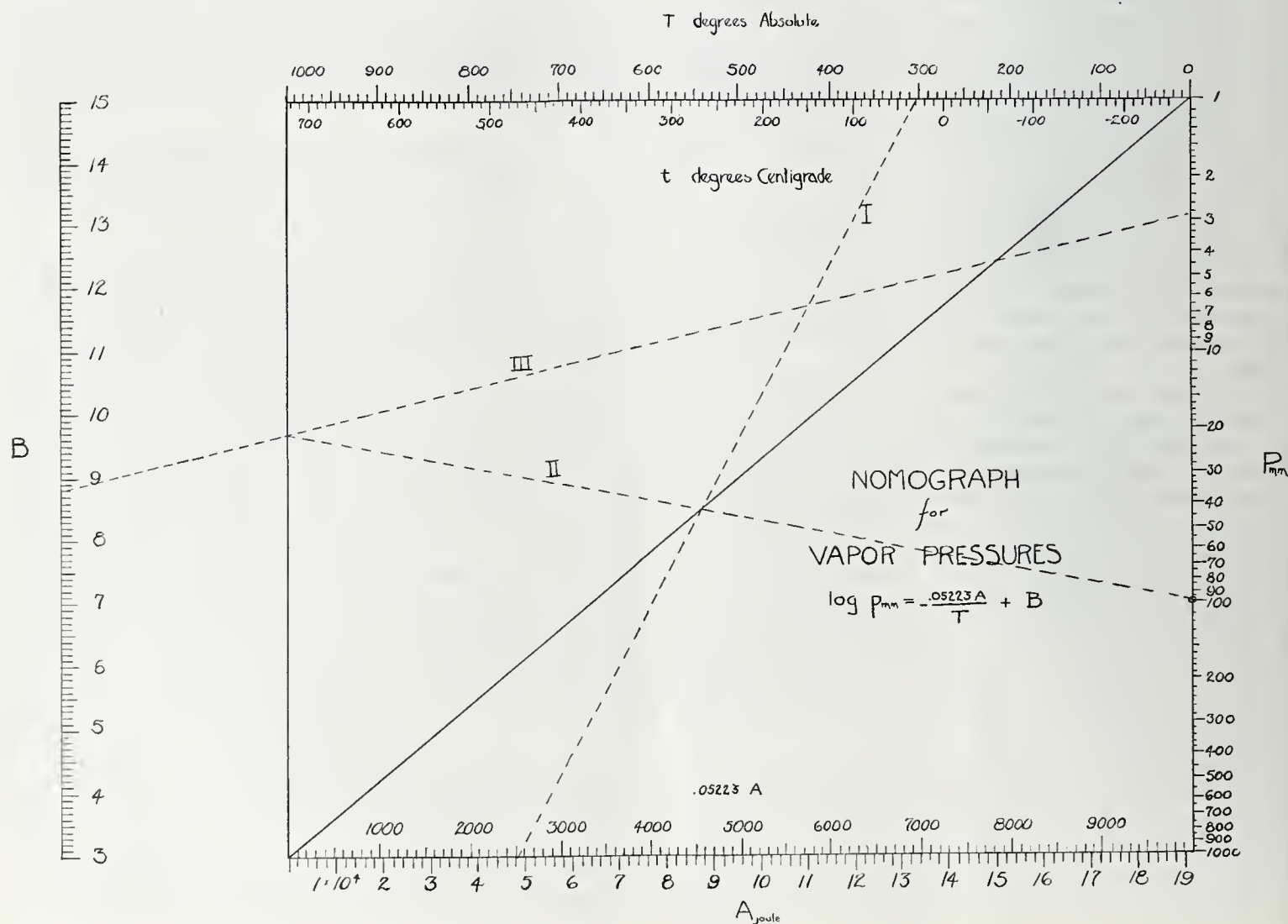
The mechanical construction of this chart is not difficult, and results from the combination of two of the type forms described by Lipka (1). Details of construction of this chart need not be discussed here, but it may be mentioned that the choice of the correct ranges for the various scales

entails considerable work in order that the scales may cover a sufficiently large range and still have the same relative accuracy.

The chart is composed of six scales, four of which are divided. These are as follows:

1. The horizontal scale at the top of the chart is the temperature scale, divided into Centigrade degrees and numbered on the upper side according to the absolute scale, on the lower in ordinary Centigrade degrees with zero at the melting point of ice; these scales are uniformly divided.

2. The horizontal scale at the bottom of the chart is graduated on both sides. The lower side, an evenly divided scale, represents the value of the constant A as given by the International Critical Tables. It must always be borne in mind that all values marked on this scale are multiplied by the factor 10^4 . For example, the location of the point 38340 is determined between the divisions marked 3 and 4 in the same manner as it would be on a slide rule. The upper side of the scale is



divided into units corresponding to 0.05223 A . Using this is equivalent to employing the equation $\log p_{mm} = C/T + B$, where C is taken as the reading on the scale in question.

3. The vertical scale at the left side of the chart represents the values of B as given by the International Critical Tables.

4. The logarithmic scale on the right side gives the value of the vapor pressure in millimeters.

5. The point 100 on the P scale, indicated by the small circle, is used as a reference point in calculating 0.05223 A/T .

6. The vertical scale without graduations would, if graduated, give values for 0.05223 A/T and C/T .

The chart is used in the following manner: Join the values of T and A by means of a straight edge, which will intersect the undivided diagonal at some point. Then join this point with the reference point on the P scale; the prolongation of this line intersects the undivided C/T scale. Finally join this intersection with the value of B and read the vapor pressure on the P scale.

This process will be made clear by a numerical example. To find the vapor pressure of isobutyric acid at 30° C., from the International Critical Table, Vol. III, page 219, we obtain the value of A as 48498 and B as 8.819. By following the procedure of the preceding paragraph the vapor pressure is found to be 2.85. This example has been worked on the chart, and the isopleths are shown by means of the

dotted lines and are numbered I, II, and III in the order in which the points are connected. Using a slide rule and a six-place log table, we obtain 2.9 and 2.877, respectively, as the vapor pressure.

From this alignment chart a reading of the vapor pressure of a substance may be made with sufficient accuracy for many purposes. If greater accuracy is desired, a larger chart with a smaller range can easily be constructed using the same principles. In any case, however, this chart will serve as a valuable aid in checking calculations. The writers wish to emphasize the fact that the large number of significant figures given in the constants A and B may be a trifle misleading, since vapor-pressure calculations are seldom made closer than one-tenth of a millimeter, except in the case of the more common substances where accurate tables have already been compiled.

A chart employing these principles and covering the range of ethyl alcohol-water mixtures is in use in the writers' research laboratories.

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Determination of Alkali in Glass

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THE reagent 8-hydroxyquinoline (1) extends the usefulness, speed, and accuracy of the Sullivan and Taylor (3) oxalate method for the decomposition of glass and the subsequent determinations of alkali, since magnesia and other interfering oxides are more readily removed from the solution of the alkalis by the organic reagent. This improved method is particularly valuable for simple borosilicate glasses of the Pyrex type and in general for silicates of not over 5 per cent alumina content which can be opened readily with hydrofluoric and oxalic acids. The use of organic reagents permits the alkalis to be weighed as chlorides. The method here described includes only the separation and determination of alkali, although attention is drawn to the usefulness of the method in removing, early in the analysis, insoluble oxalates (2) and quinolates, thus making it possible to determine more speedily these oxides, lime, magnesia, and alumina.

DECOMPOSITION OF SAMPLE

As in the original Sullivan and Taylor method, a 1-gram, or larger, sample of the ground glass is placed in a platinum crucible of 40 cc. capacity. The glass sample is moistened with water, 2 grams of oxalic acid and 20 cc. of 48 per cent hydrofluoric acid added, the contents stirred with a platinum

THE SULLIVAN and Taylor oxalate method with the additional use of 8-hydroxyquinoline is particularly suited for alkali determinations in borosilicate glasses and has additional uses in determining lime, alumina, and magnesia on the same sample. These determinations can readily be made in one day. Larger samples can be used for alkalis, a point of advantage in low-alkali glasses and glasses containing small amounts of lime, magnesia, and alumina, etc., in determining their oxides. The method is not recommended for glasses of over 5 per cent alumina or materials of the feldspar class.

Double precipitation of the oxalates and quinolates is recommended for accurate alkali determinations. This practice corresponds with that of the J. Lawrence Smith method in double precipitation or treatment of precipitates.

wire or stirring rod, then evaporated to dryness (preferably in the special radiator described in the original method) at a temperature just high enough to expel the excess of oxalic acid. Before the end of evaporation a loosely fitting platinum cover should be placed on the crucible to guard against possible spattering. When all of the acid has been expelled, the crucible is cooled and the evaporation repeated once or twice more with oxalic acid and water, depending upon the alumina content of the glass. The amount of oxalic acid used is about 5 grams, and should be noted for the blank determination.

REMOVAL OF PRECIPITATES

OXALATE. After the last evaporation, when all of the oxalic acid has been expelled, the remaining oxalates are taken up with hot water, allowed to cool, and filtered. The amount of water used for taking up the oxalates, washing the precipitate, etc., usually amounts in all to not over 100 cc., and the crucible may be used to advantage as the extraction container, the filtrate being caught in a Pyrex beaker of 150 to 250 cc. capacity.

At this stage, with a borosilicate glass free from lead and second-group elements, no filtration is necessary to remove insoluble oxalates unless the small amounts of these elements, present as impurities, are to be determined. The 8-hydroxy-

quinoline reagent may be added directly to the total extraction from the crucible. With a lime or lead glass, however, the insoluble oxalates are filtered out and for accurate analysis dissolved in hydrochloric acid. The usual oxalate precipitation is then made after adding a few crystals of oxalic acid followed by enough ammonia to cause the solution to become ammoniacal. The second filtrate is treated separately with 8-hydroxyquinoline reagent and may contain no insoluble quinolates, in which event it is saved for the final evaporation.

QUINOLATE. The original oxalate filtrate or the entire unfiltered extraction from the last crucible evaporation, amounting to about 100 cc., is ready for the quinolate precipitation. A 5 per cent solution of 8-hydroxyquinoline in ethyl alcohol is used as reagent, from 10 to 20 cc. being required depending upon the amount of oxides to be precipitated as quinolates. The reagent in excess will color the supernatant liquid yellow. Too large excess of precipitant should be avoided as it must be destroyed later. After the addition of reagent, the cool solution is made slightly ammoniacal dropwise with stirring, and allowed to stand in the beaker cooled by tap water for at least one-half hour.

Filtration is then made using 1 per cent ammonia and a trace of the precipitant in the wash water. The filtrate is caught in a platinum dish and evaporated to dryness. The filtrate from the reprecipitation of oxalates is also added to the contents of the platinum dish, provided no insoluble quinolates are found present. In addition, it is advisable for accurate work to reprecipitate the regular quinolate precipitate. The precipitate is dissolved in hydrochloric acid, excess 8-hydroxyquinoline added, and the solution made ammoniacal followed by cooling for one-half hour and filtration.

REMOVAL OF ORGANIC MATTER AND CONVERSION TO ALKALI CHLORIDES

The evaporated contents of the platinum dish are gently heated by passing the flame across the bottom of the dish until the organic matter and ammonium salts have been removed. The final stage of this decomposition is noted at just under a red heat when the alkali oxalates bubble slightly, then remain as a quiet film of alkali carbonates.

A cover glass should be placed on the dish upon cooling. After dissolving the carbonates in a little water and adding a few drops of hydrochloric acid, heat is applied again with the cover glass in place for a minute or two until the evolution of carbon dioxide and danger of loss of solution by entrainment is over. In about 5 to 10 minutes the dish is dry and the contents are again taken up in a little water. Any organic char or silica is filtered out and the solution evaporated to dryness in a weighed platinum dish. Washington's (4) suggestion of adding a few drops of alcohol as dryness is approached is found to be excellent in causing the alkali chlorides to come down in such a form that decrepitation dangers are considerably lessened. The dish containing the alkali chlorides is gently ignited with a cover glass in position, being careful to keep below a dull red heat. The alkali chlorides are weighed as sodium chloride and potassium chloride, and the usual potash determination can now be made and the sodium oxide determined by difference.

A blank should be run on the method. On a 1-gram sample it was found that this blank amounts to 1 mg. of sodium chloride. Based on experience, the blank of the oxalate quinolate method is equivalent to only one-quarter that of the J. Lawrence Smith method under comparable conditions.

Results with some Bureau of Standards glass samples are shown in Table I using the method just described on 1-gram samples and comparing the weights of alkali chlorides thus

found with the equivalent chlorides of the recommended bureau analyses.

TABLE I. COMPARISON WITH BUREAU OF STANDARDS VALUE

GLASS	(1-gram sample used)			
	BUR. STANDARDS VALUE	OXALATE QUINOLATE METHOD	DIFFERENCE	
	Gram	Gram	Wt. of alkali chlorides Gram	Na ₂ O in glass %
Bureau No. 8 (soda-lime magnesia glass)	0.3141	0.3138	-0.0003	-0.02
Bureau No. 89 (lead barium glass)	0.2406 0.2406	0.2416 0.2396	+0.0012 -0.0010	+0.06 -0.05

Some results on other glass samples analyzed in this laboratory using both the quinolate and J. L. Smith determinations are given in Table II.

TABLE II. COMPARISON WITH J. LAWRENCE SMITH METHOD

GLASS	(1-gram sample used)			
	J. LAWRENCE SMITH	OXALATE QUINOLATE	WT. OF ALKALI CHLORIDES	Na ₂ O IN GLASS
	Gram	Gram	Gram	%
1. Sodium borosilicate	0.0926	0.0930	+0.0004	+0.02
2. Sodium borosilicate	0.0610	0.0601	-0.0009	-0.05
3. Lead borosilicate	0.0848	0.0840	-0.0008	-0.04
4. Barium calcium silicate	0.3400	0.3394	-0.0006	-0.03
5. Bureau No. 91 (CaF ₂ opal not standardized)	0.2114	0.2100	-0.0014	-0.07
Bureau No. 91	0.2116	0.2098	-0.0018	-0.10

EXPERIMENTAL PROCEDURE

In order to study methods of separating alkalies from other elements remaining in solution after decomposing ordinary glasses, standard solutions were made up of the chlorides of aluminum, calcium, magnesium, sodium, and potassium. These solutions were tested by known methods for content of added constituent and for impurities of the other salts. The quinolate determination of alumina and magnesia gave very satisfactory checks with the ammonia and phosphate gravimetric analyses, respectively. The alumina as determined on 5 cc. of the aluminum chloride solution was exactly 0.0118 gram by each method. Magnesia by gravimetric pyrophosphate determination, in 5 cc. of magnesium chloride solution, was 0.0091 gram, whereas by the quinolate gravimetric determination it was 0.0089 gram.

This sample of synthetic solution was equivalent to:

	Grams
NaCl	0.0625 (0.0010 gram NaCl in 1-gram glass sample to 0.053% Na ₂ O)
KCl	0.0602
Alkali chlorides	0.1227
MgO	0.0090
CaO	0.0256
Al ₂ O ₃	0.0118
H ₂ C ₂ O ₄	2.0000

Evaporation to dryness in a platinum dish was followed by fuming off the excess oxalic acid at 150° C. Duplicate samples were run by the new method without double precipitation of the oxalate or quinolate precipitates. These analyses showed errors of -0.0043 and -0.0030 gram of alkali chlorides, or on a 1-gram glass sample -0.25 and -0.16 per cent sodium oxide.

Starting with fresh samples, using a single oxalate and double quinolate precipitation, errors of -0.0029 and -0.0019 gram of alkali chlorides were obtained. These errors on a 1-gram glass sample would be equivalent to -0.15 and -0.10 per cent sodium oxide.

Another sample was run using a double oxalate but single quinolate precipitation, and this showed an error of 0.0020 gram of alkali chlorides, or on a 1-gram sample of glass -0.11 per cent sodium oxide. Leaving out the calcium chloride solution and running still another sample of solution,

omitting the oxalate separation and with a single quinolate precipitation, resulted in an error of -0.0023 gram of alkali chloride. A determination using no calcium chloride solution and omitting the oxalate precipitation but with a double quinolate precipitation, gave an error of -0.0004 gram of alkali chloride.

These results indicate that it is desirable to reprecipitate both the oxalate and quinolate precipitates for accurate alkali determinations. The same applies to the J. Lawrence Smith determination, for it is extremely important to reprecipitate the calcium carbonate formed by ammonium carbonate, as otherwise a loss of several milligrams of alkali chloride may be suffered.

It is found that boric oxide is eliminated with the silica in the attack of the sample by hydrofluoric acid and oxalic acid, and that traces of fluorides remaining after the evaporations do not interfere in the separations.

Sulfates when present may be removed with barium chloride and the barium removed as quinolate.

Methods for determining the other oxides are not given, but references are given to articles describing the use of 8-hydroxyquinoline.

ACKNOWLEDGMENT

It is a pleasure to record here appreciation of the interest and helpfulness of W. C. Taylor, chief chemist of the Corning Glass Works, in the work on this problem, and to acknowledge the helpful information obtained from G. E. F. Lundell of the Bureau of Standards.

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The Bleaching Earths

A Laboratory Study

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CERTAIN igneous rocks, such as granite, basalt, dunite, diabase, and many others, when exposed to weathering gradually break down both physically and chemically, the ultimate solid residue of the more profound types of weathering being largely inactive clays and soils. The original rock was composed of silicates high in bases, whereas the end products are secondary silicates, low in the more soluble bases but high in the oxides of iron and aluminum, and in silica.

Midway on the decomposition curve are the products that are typical of the active bleaching or filtering earths. Some of our best fuller's earth deposits are probably only the accumulated wash of partly decomposed igneous rocks which for some reason has not gone to soil or to inactive clay—typically the white and refractory clays. In a thoroughly weathered and partly leached condition, simple drying at 160° to 190° C. is sufficient to drive off adsorbed water, leaving the free valencies or open bonds essential to the bleaching or filtering action. When the leaching is less profound, acid treatment may greatly increase bleaching power.

Some igneous dikes in Arkansas (1) decomposed *in situ* show decomposition to bleaching earth, to inactive ceramic clays, and to bauxite in neighboring parts of the same dike. Where the original rock was composed largely of the highly basic and complex minerals augite, hornblende, biotite, and (or) nontro-nite, the weathering was to fuller's earth which was formerly mined and shipped. Where it was feldspar, it has decomposed to kaolin, and where it was nepheline it is becoming bauxite. Here in Washington are exposures of decomposed granite showing the three chief products just described within a few yards. Near Bull Run, Virginia, is a decomposed diabase having excellent bleaching properties after sifting and acid-leaching.

Only sedimentary deposits of bleaching clay are now being worked in this country, since these are abundant and the expense of screening is avoided. The chief sources are Georgia, Florida, southern Illinois, Texas, Colorado, Utah,

Nevada, Arizona, and southern California. Several plants mine and mill as much as 10,000 tons per month. There is no production from glaciated areas. The bleaching clays were apparently brought down in large quantities of fresh water which kept the clay particles at or near their isoelectric points. Thus, soluble bases were removed from their surfaces (and replaced by H and OH) but not completely from their interiors. Complete leaching of minerals low in iron, with long contact with fresh water, would result in kaolin. The western bleaching clays are less leached, and a few of them of the bentonite type require an acid leach to activate them.

PROPERTIES OF EARTH

Neither chemical composition nor molecular structure as determined by x-ray analysis is sufficient to decide whether a mineral will be an active bleaching agent, since bleaching depends primarily on the condition of the surface rather than directly on composition or internal structure. The filtering material may be a simple hydrous oxide, a silicate, a glassy slag, ordinary glass, or volcanic ash. Activation may be said to consist in opening up the bonds over the surface (pores included) and the activity depends upon the extent of activated surface or number of open bonds per unit mass. As the writer has shown, it is possible to produce iron oxide, aluminum oxide, and silicon dioxide (2) in forms so active as to crack paraffin, and to activate the surface of even sea sand and crushed quartz crystals (3). Among the commercial fuller's earths, activities sufficient to crack paraffin, gasoline, or even the highly purified laxative oils are the rule.

The bleaching or filtering action (decolorizing and deodorizing, chiefly) of the active earths on oils and other solutions varies greatly with the solution that is to be filtered and with the filtering material used. Hydrocarbons like petroleum, which contain no OH groups, require the assistance of heat to drive the OH from the filtering material. Either the earth is first heated to 180° C. (160° to 200° C.) and then used dry, or

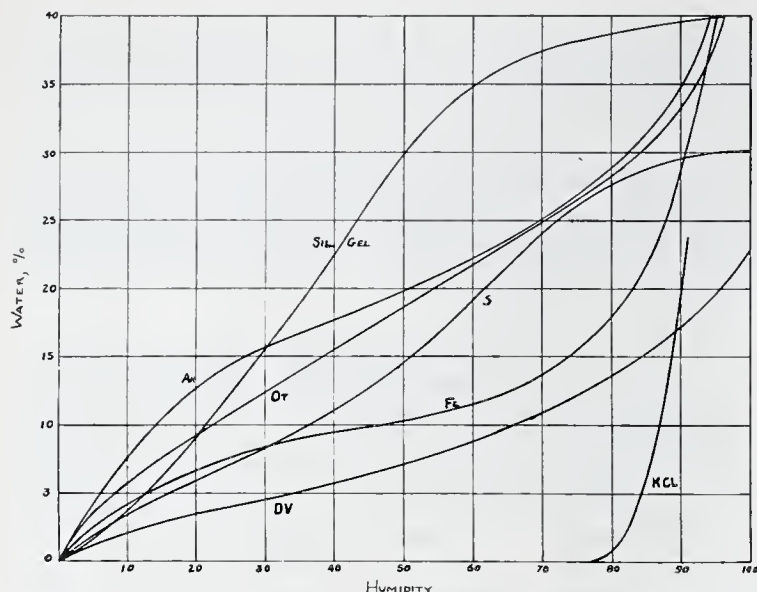


FIGURE 1. WATER CONTENT AT VARIOUS HUMIDITIES AT 26° C.

FL, raw Floridin from Quincy, Fla.
DV, raw clay from Death Valley, Nev.
Ar, raw clay from Chambers, Ariz.
Ot, bentonite (Otaylite) from Otay, Calif.
Sil/Gel, powdered
KCl, powdered
S, powdered serpentine, acid treated, active

else it is heated to a similar temperature after oil and moist earth are mixed (the usual procedure). On the other hand, such fluids as fish and vegetable oils, animal fats, and fruit juices, containing OH and with room for more, are filtered by moist and slightly basic filters, for their stronger ions can displace H and OH from the filter surfaces without the assistance of heat. Even a little base left in the filter is not objectionable. One neutral clay, filtering both hydrocarbons and animal fats about equally well, is composed of silicon dioxide, 69; iron or aluminum oxide, 16; calcium or magnesium oxide, 2; and potassium or sodium dioxide, 2.5 per cent, the rest chiefly water. In many special cases doubtless secondary reactions occur. Some clays even remove the odor and taste from fish oil. Mercaptans and sulfonic acids are removed from petroleum by certain clays. Palm oil is said to be the most difficult to decolorize completely, and crude petroleum is perhaps the easiest.

INVESTIGATION OF COMMERCIAL EARTHS

A list of the principal clays investigated is given below, together with tables of the more significant data obtained, some of which are graphed in the figures.

PRINCIPAL CLAYS EXAMINED

1. Attapulugus, Ga. Courtesy Attapulugus Clay Co., Philadelphia, Pa.
2. Macon (Pikes Peak), Ga. General Reduction Co., Macon, Ga.
3. Quincy, Fla. "Floridin." Floridin Company, Warren, Pa.
4. Ocala, Fla. The Superior Earth Company, Ocala, Fla.
5. Creede, Colo. "Kontak." Peerless Clay & Minerals Co., Chicago, Ill.
6. San Antonio, Tex. The Standard Fuller's Earth Co., San Antonio, Tex.
7. Olmstead, Ill. The Sinclair Refining Co., Olmstead, Ill.
8. Aurora, Utah. Western Clay and Metals Co., Aurora, Utah.
9. Aurora, Utah. Western Clay and Metals Co., Aurora, Utah.
10. Death Valley, Nev. "Palex." D. V. Clay Co., Coen Companies, Inc., Los Angeles, Calif.
11. Tehachapi, Calif. "Filtrol." Filtrol Company of Calif., Los Angeles, Calif.
12. Chambers, Ariz. "Filtrol." Filtrol Company of Calif., Los Angeles, Calif.
13. English Fuller's Earth, Brand XL, purchased.
14. Japanese Acid Clay through Yoshio Tanaka, Tokyo, Japan.
15. D. C. Decomposed Granite, greenish gray, screened, Thirty-third St. and Broad Branch Road.

16. D. C. Decomposed Granite, ash gray, Nebraska Ave. and Rock Creek Ford Road.

17. Weathered Dunite, yellow, Webster, N. C. Decomposed olivine.

The clays are listed in Table I in two classes, those for filtering mineral oil, chiefly petroleum lubricants, and those used chiefly for cotton oil, palm oil, fish oil, and lard, which contain OH. The filtering data given in the second and third columns for untreated and acid-treated clays are the volume of oil completely filtered to water-white relative to the volume of the clay filtering it. These numbers are only slightly related to commercial value, since it is the yellow and red fractions that are desired in many cases.

The water content of the clay when in equilibrium with air at 20 and 80 per cent relative humidity and about 26° C. are given for both raw and treated clays. These are relative to the ignited weight as base, whereas similar data in Table II are referred to weight at zero humidity (over P₂O₅) as base. Acid treatment in general lowers moisture retention.

The solution obtained by treating each clay 15 hours with hot dilute hydrochloric acid was roughly analyzed for iron, aluminum, calcium, and magnesium, the clay thoroughly washed free from chlorides and again brought to room humidity and weighed, the loss in weight being given as acid soluble ranging from 10 to 40 per cent. The soluble portion is chiefly iron and aluminum, but in two cases is iron and magnesium.

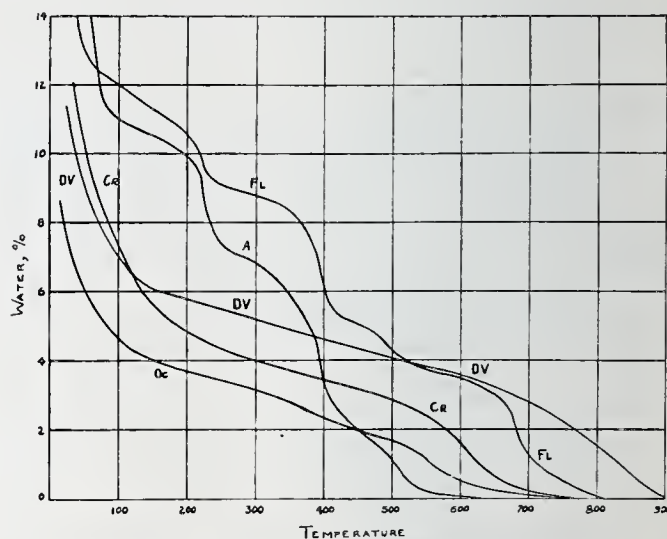


FIGURE 2. WATER AT VARIOUS TEMPERATURES

DV, Death Valley
Cr, Creede
FL, Floridin
Oc, Ocala
A, Attapulugus

In the last six columns (Table I) are given weight percentages of water retained by untreated clays at various temperatures. Since the removal of water not retained at 50° C. is not likely to result in open bonds, and since heating to 200° C. is sufficient to activate a clay, the loss of water between 50° and 200° C. should be a measure of the true absorbing power of clays. The correlation is quite good. The outstanding exception is the Death Valley clay, but this is an impure magnesium silicate.

A few hydration curves are shown in the figures. The weight-humidity curves of Figure 1 are from weights when in equilibrium with carefully checked sulfuric acid solutions in closed vessels. The equilibrium weights taken at eight points are repeatable and reversible, but equilibrium is reached so slowly that only a few complete curves were run on commercial clays.

The weights plotted are related to the base weight at zero humidity, which exceeds the ignited weight by something

TABLE I. PROPERTIES OF BLEACHING EARTHS

CLAY	TYPE	WHITE BLEACH		WATER CONTENT AT:				ACID SOLUBLE	—SOLUBLE PORTION—				WATER RETAINED AT:					
				20%	80%	20%	80%		Fe	Al	Ca	Mg	50°	100°	200°	300°	400°	600°
		Raw	Treated	Raw	Treated	C.	C.	C.					C.	C.	C.			
		%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	
Attapulgius	Min	0.8	0.5	18.9	32.6	9.3	21.6	18.6	4	4	1	1	14.2	11.0	10.9	6.7	3.5	0.4
Macon	Veg	0.5	0.9	13.2	24.8	7.0	19.8	20.8	6	2	2	Trace	12.8	7.4	5.6	5.2	4.7	2.4
Quincy	Min	0.7	0.6	19.5	29.6	14.8	24.6	25.6	4	3	3	Trace	15.6	12.4	10.4	8.8	6.4	3.5
Ocala	M&V	0.6	0.9	8.9	18.7	3.9	9.8	28.1	3	4	3	Trace	8.1	4.5	3.7	3.1	2.3	0.5
Creede	M&V	0.8	1.2	12.4	23.3	16.4	25.5	11.1	6	3	1	0	10.4	7.2	4.8	4.0	3.4	0.3
San Antonio	Min	0.7	1.1	11.0	21.8	6.9	13.9	11.1	6	3	1	Trace	7.5	5.9	4.7	4.4	3.9	1.5
Olmstead	Min	0.6	0.3	13.9	26.2	14.3	27.3	23.3	7	3	0	Trace	6.9	5.8	4.6	4.1	3.4	1.6
Aurora	Min	1.4	1.2	15.6	30.8	11.3	23.5	10.9	4	3	2	1	10.8	6.1	4.6	4.1	3.6	2.2
Aurora	Veg	1.1	1.2	18.8	28.9	9.8	19.8	9.8	4	4	2	Trace	12.2	6.4	4.5	4.0	3.5	1.4
Death Valley	Min	1.8	1.2	11.6	24.8	7.1	19.2	24.9	Trace	1	1	8	9.2	6.9	5.7	5.1	4.6	3.5
Tehachapi	Veg	1.1	1.1	14.6	22.9	12.3	22.3	13.1	4	4	Trace	2	12.6	8.4	6.2	5.0	4.3	2.1
Chambers	Min	0.6	2.0	26.5	36.5	21.3	44.8	22.6	5	4	1	Trace	14.8	11.6	5.7	5.2	4.7	2.8
English	M&V	1.2	2.0	21.0	29.7	9.3	22.7	19.9	5	4	1	Trace	14.2	8.0	5.3	4.7	4.1	2.2
Japanese	M&V	1.0	1.1	16.1	27.2	7.3	38.7	14.2	3	6	1	0	14.3	7.0	5.2	4.6	3.9	1.7
D. C. Granite	Min	0.0	1.5	17.3	21.9	13.0	26.5	32.6	8	2	Trace	0	7.0	4.5	3.8	3.5	3.3	0.5
D. C. Gray	Min	0.4	1.0	6.3	7.8	4.6	10.5	13.7	5	5	Trace	Trace	5.5	4.6	4.2	3.9	3.8	0.8
Dunite	Min	1.2	1.2	16.1	25.8	12.5	26.6	40.0	5	0	0	5	13.4	9.7	9.1	7.6	6.7	1.3

more than the water of constitution and of crystallization. The interesting part of these curves is the upper end where saturation is approached. Two distinct types are apparent. The complex clays and the potassium chloride ascend steeply to high values as saturation is approached. Such minerals cake on drying from a saturated condition. Clays of this type lose water in a saturated atmosphere when in muddy condition or even when covered with a millimeter of clear water. If a hard dry lump and a thin mud of the same clay are put in the same saturated atmosphere, they approach the same equilibrium water content in a year or two in a very moist but firm condition resembling that of the original wet clay as mined. On the other hand, the amorphous oxides of silicon, aluminum, and iron (see Table II) reach a definite maximum. The acid-treated serpentine gives a curve of the same type, since it has been reduced to open-bonded silica.

TABLE II. WATER CONTENT OF CLAYS AT VARIOUS RELATIVE HUMIDITIES

Humidity, %	10	20	30	50	70	80	90	95	98
Quincy	4.2	6.9	8.4	10.2	13.8	17.9	28.6	39.7	46.7
Death Valley	2.1	3.3	4.2	7.0	11.2	14.0	17.0	19.3	21.2
Chambers	7.5	12.8	15.8	19.3	25.0	29.2	34.7	41.1	44.8
Otaylite	6.0	9.1	12.2	18.8	25.1	28.3	33.5	38.4	44.0
Silica gel	3.5	9.0	15.4	30.3	37.4	38.7	39.6	40.0	40.4
KCl	0.0	0.0	0.0	0.0	0.0	0.7	19.7	39.5	..
Serpentine	3.6	6.0	8.4	14.4	24.2	27.8	29.8	31.2	31.3
Al ₂ O ₃ (Am)	4.8	6.9	8.4	14.4	24.7	29.8	33.0	34.0	34.4
Fe ₂ O ₃ (Am)	3.9	6.0	8.2	13.4	16.1	16.9	17.5	17.6	17.8
"Cr Sil."	2.2	3.2	4.1	6.1	10.0	17.8	38.1	55.2	..

In Table II are given the data of the curves of Figure 1 with some others added for comparison. The Otaylite is a true bentonite having no filtering power even after acid treatment, yet its humidity curve parallels that of the Chambers earth rather closely. The amorphous oxides were prepared in this laboratory. The "chromium silicate" was from a gel formed by chromic acid and is noteworthy for its low retention of water at low and moderate humidities but very high retention approaching saturation. There are no shoulders on any of these curves as there are on some of the weight-temperature curves.

A few hydration-temperature curves are reproduced in Figure 2. The equilibrium is perfectly definite and reproducible from any given clay stock, but acid treatment or even boiling in water affects some of the curves profoundly. The water is completely reversible up to about 200° C., and irreversible above 600° C. Between these temperatures clays differ considerably in reversibility. Attapulgius and Floridin are extreme in the amount of water held up to 350° C. and in having pronounced shoulders. Ocala presents the opposite extreme of low, smooth curve. All the other curves lie between Ocala and Floridin and are mostly smooth and regular. Acid treatment of a clay lowers and smooths its dehydration curve to one similar to Ocala.

In Figure 3 are shown thermal dehydration curves of some

closely related compounds for comparison. Some of these have been studied by Tanaka (4) and others. The iron oxide, permutite, and chabazite curves are smooth and regular, but that of silica gel is distinctly wavy. The decided bow on the aluminum oxide curve between 200° and 400° C. is characteristic. The dehydration curves of many active clays lie near that for silica gel.

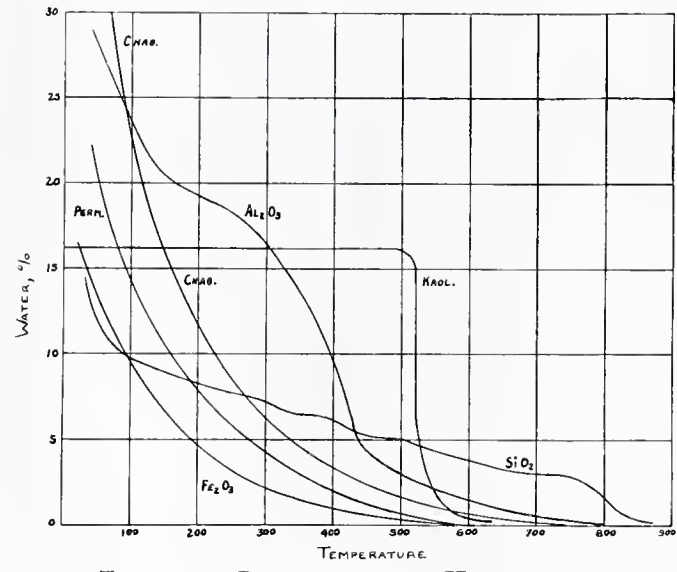


FIGURE 3. DEHYDRATION OF HYDROXIDES
Fe₂O₃ from Fe(OH)₃
Al₂O₃ from Al(OH)₃
SiO₂ from Si(OH)₄
Permutite
Chabazite
Kaolinite

ACKNOWLEDGMENT

Sincere thanks are due for the whole-hearted coöperation of the many producers of clays for freely supplying materials and information and for permission to visit their mines and plants. The author is greatly indebted to C. S. Ross for much helpful criticism.

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NITROGEN FIXATION PLANT NEAR JOHANNESBURG. What is claimed to be the first nitrogen fixation plant in the Southern Hemisphere is nearing completion at Modderfontein, a few miles outside Johannesburg. The cost is estimated at half a million pounds and it is claimed that this unit will be instrumental in making the southern part of Africa independent of foreign products.

Fractionating Column for Use under Diminished Pressure

M. T. BUSH AND A. M. SCHWARTZ, *Cornell University, Ithaca, N. Y.*

ALTHOUGH there are many columns described in the literature, there are none suitable for general use under diminished pressure, and the separation of liquids by fractional distillation *in vacuo* is regarded as an arduous task in many organic laboratories. It is the purpose of this paper to describe a complete fractionating apparatus which is efficient under a wide variety of conditions.

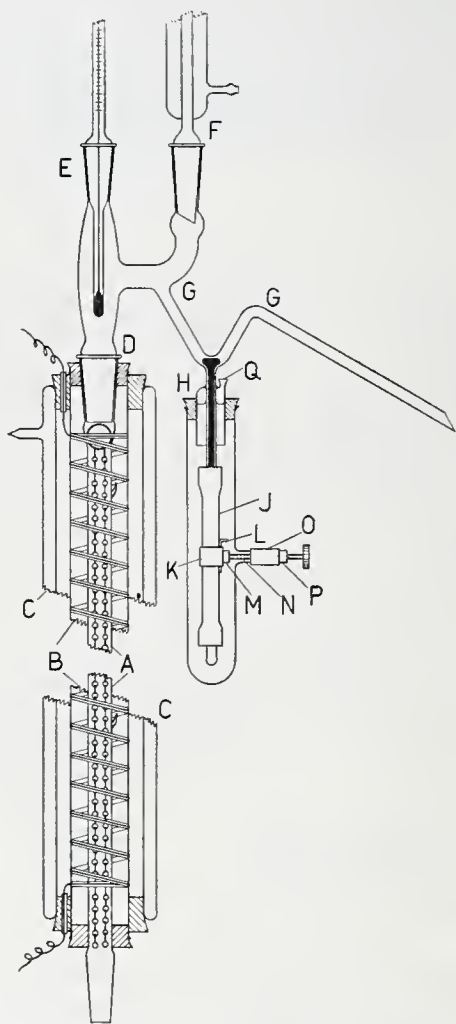


FIGURE 1. FRACTIONATING COLUMN AND MODIFIED FLOW DIVIDER

Perhaps the greatest difficulty in the operation of a still is to provide adequate insulation. When distilling at atmospheric pressure it is often possible to do this by wrapping the column with "85 per cent magnesia." When operating under relatively low pressure, however, there is excessive condensation, and if the column is as much as 2 to 3 feet (50 to 76 cm.) long it is not possible to distil satisfactorily at temperatures above 80° to 100° C. with either magnesia or an evacuated jacket as insulation. This difficulty is removed by using a heating unit in conjunction with an evacuated jacket.

In the drawing, Figure 1, the Pyrex tube B (30 mm. in diameter) is secured within the evacuated jacket C (45 mm. internal diameter) by means of rubber stoppers. The heating is accomplished electrically with a helix of chromel wire on a narrow strip of asbestos paper, fastened at the ends with copper wire. About fifty turns of chromel are convenient for a 3-foot

(50-cm.) column. The visibility afforded by the glass insulation allows control of the heating by means of thermometers which are tied to small glass hooks on the column. The column itself may be either the Vigreux or the filled type. The authors have had success with a 12-mm. tube filled with small jack-chain by hanging two or three lengths from a metal ring at the top (A).

The mercury valve of the flow divider (2) has been simplified by surrounding the rubber tube with mercury thus making it leak-proof. The heavy-walled rubber tube J (3 by 6 mm.) is slipped over the valve stem, the steel collar K (1 cm. wide), fitted with the nut M, is slipped on, and the open end of the tube is plugged. The rubber-to-glass connections are sealed with shellac. The steel plate L (8 mm. wide) is put in place and the side-arm test tube adjusted as shown. The screw N, with the nut P adjusted, is then connected with the nut M through the side arm and the rubber tube O. The valve is filled with mercury through the opening at F and the tube G, and the test tube, H, is filled with mercury through the funnel Q. With this arrangement the tube does not leak at a pressure of 1 mm. It is well to scrub out the tube J before putting it in place to facilitate the removal of adsorbed air.

The most satisfactory receiver for cutting off fractions of distillate is a slight modification of the Bredt-Parlatosche "Star" (1), in which the receivers are either bulbs or test tubes. This avoids contamination of the distillate by stoppers or stopcock grease.

After the apparatus is once assembled it is not difficult to run a fractionation. The column is first warmed to about 5° below the initial boiling temperature, and the flask, carrying a very fine capillary ebullition tube, adjusted at the bottom. The rate of distillation is controlled by the tempera-

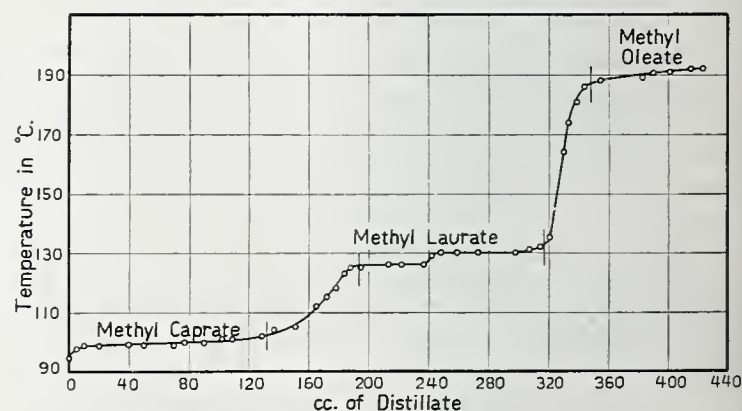


FIGURE 2. TYPICAL FRACTIONATION CURVE

ture of the heating bath. It is necessary, of course, to heat the column more strongly as the temperature of the distillation rises. The amount of reflux is adjusted, and the fractions taken according to the readings on the thermometer.

To indicate the efficiency which can be expected from this column, a typical fractionation curve is given in Figure 2. The mixture of esters obtained in the examination of a natural oil was fractionated at 8 mm. and the fractions cut as indicated. The methyl caprate and methyl laurate fractions were relatively pure, but the methyl oleate apparently contained some linoleic and linolenic esters, which explains the

continuous slope of that portion of the curve. The abrupt rise in temperature in the middle of the laurate fraction is due to an increase in the rate of distillation. The 60-cc. intermediate between the caprate and laurate fractions was carefully refractionated into 22 cc. at 92° to 93° C., 10 cc. at 93° to 115° C., and 23 cc. at 115° to 117° C., at a pressure of 5 mm.

The apparatus can be used conveniently for amounts of material from 50 to 400 cc. having a boiling point up to about 200° C., at pressures down to 1 mm. It is most conveniently assembled with the aid of standard ground-glass connections, as indicated in Figure 1. The size of the connection at *E* is

number 9.5, at *F* number 11, at *D* number 15, and at the bottom of the column number 11. For temperatures above 150° C. it is well to insulate the flow divider with "85 per cent magnesia."

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RECEIVED July 6, 1931.

Wet Microcombustion of Organic Compounds

With Particular Reference to Cellulose Derivatives

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IN A communication to be published in a later issue, the writer discusses the application of a strong oxidizing mixture upon cellulose compounds, and by using a specially designed apparatus, estimates the carbon content by the pressure exerted by the carbon dioxide formed. However, it is sometimes necessary to perform analyses using samples smaller than 0.10 gram, and as the sample size is reduced, the efficiency of the above method decreases. It was considered possible that by using a standard solution of the oxidizing reagent, a much smaller sample could be determined by using volumetric methods. Such a method has apparently been obtained.

As an oxidizing reagent, a mixture of a concentrated aqueous solution of potassium dichromate and concentrated sulfuric acid was used. This mixture performed exceedingly well with most of the samples used, but some were found which resisted "wetting" to such an extent that it was necessary to boil the mixture for a relatively long time in order to consume the sample completely. Such a procedure did not commend itself to accuracy. A solution of chromic acid anhydride in c. p. phosphoric acid gave the necessary qualifications in that it consumed all the samples used, and since it contained no unnecessary water, steam was not released on subsequent heating.

A special form of apparatus, shown in Figure 1, was designed for this method, the design given being the result of experimenting with many other forms of apparatus.

The oxidizing reagent is prepared by dissolving one part by weight of c. p. chromic acid in nine parts by weight of c. p. sirupy phosphoric acid. A more concentrated mixture may be used if desired. Approximately 15 cc. of the oxidizing reagent are run into the reaction flask, *A*, by means of a standard buret. It is suggested here that where a considerable number of analyses are made, a small buret capable of delivering about 15 cc. be constructed for use in this method.

Twenty cubic centimeters of 0.05 *N* barium hydroxide solution are run into flask *B* from a constant-delivery buret. The sample (0.0050 gram or less), previously weighed in a piece of platinum foil, is introduced into the reaction flask. A very slow stream of dry air, which has been washed free of carbon dioxide, is conducted through the apparatus and a gentle heat is applied to flask *A*, using a microburner. When the reaction has ceased, the air should be continued to pass for a reasonable length of time. The apparatus is disconnected and the barium hydroxide solution is washed and precipitated into a beaker, a drop of phenolphthalein indicator

is added, and the excess hydroxide rapidly titrated with 0.05 *N* hydrochloric acid.

The acid mixture in flask *A* is washed into a 250-cc. volumetric flask and made up to mark with distilled water. A 25-cc. portion is aliquoted and transferred to a beaker. To this 20 cc. of 20 per cent potassium iodide solution are added and the liberated iodine is titrated with 0.1 *N* sodium thiosulfate solution using starch solution as an internal indicator.

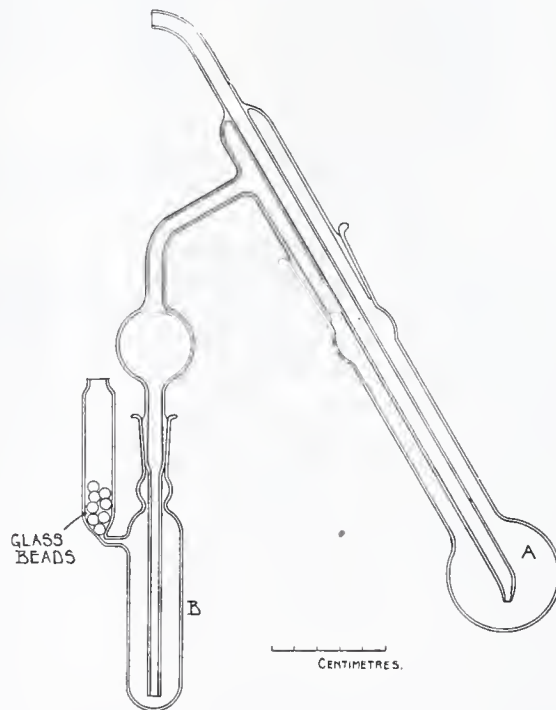


FIGURE 1. SPECIAL APPARATUS FOR MICROCOMBUSTION

A blank determination is made upon the equivalent amounts of oxidizing reagent and barium hydroxide used. In the latter, the blank determination would adjust an error due to possible contamination by carbon dioxide during transferring of the solution. The actual titration subtracted from the blank titration gives the amount of reagent entering into the reaction. From each of the above results, the per cent carbon present in the sample is obtained, one depending upon the amount of carbon dioxide formed, and the other upon the amount of oxygen consumed.

1 cc. of 0.05 *N* NC_2 = 0.0003 gram of carbon
 1 cc. of 0.1 *N* $\text{Na}_2\text{S}_2\text{O}_3$ = 0.0008 gram of oxygen

The writer has used this method for a considerable time and found that for all practicable purposes one need only consider the barium hydroxide titration for calculation of results, the other being merely a check.

$$\frac{(\text{cc. of blank} - \text{cc. of actual titration}) \times 0.0003 \times 100}{\text{weight of sample}} = \% \text{ carbon}$$

It is self-evident that absolute cleanliness is necessary in using this method. Before each series of runs, the flasks should be thoroughly cleaned with cleaning solution, washed well with distilled water, and dried in an oven.

RECEIVED July 14, 1931.

Rapid Method for Fixing End Point of Potentiometric Titration

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IN THE ideal case, the end point of an electrometric titration is so sharply defined by a considerable change in potential with the appearance of a very slight excess of the titrating agent that it may readily be located either by merely observing the point of most rapid change in potential as the titrating solution is added, or by determining the position of the vertical portion covering the inflection of the curve obtained by a simple plot of potential versus volume of titrating solution. There are, however, many factors which tend to flatten the titration curve and thus obscure the inflection that marks the end point. For example, in oxidimetric reactions a relatively small difference in oxidation potential between the oxidant and reductant has this effect; in precipitation reactions the titration curve flattens rapidly with slightly increased solubility of the precipitate; in acidimetric reactions the effect of a high concentration of neutral salt is more noticeable under most conditions than in the other types of titration, and the magnitude of the dissociation constants of the acids and bases involved determines the clarity of the end point.

Figure 1 illustrates the pronounced decrease in the slope of a neutralization curve caused by a high salt concentration. Curve 1 is the titration curve of 0.004 *N* sulfuric acid with sodium hydroxide. Curve 2 shows the same titration carried out in a solution 1.5 *M* with respect to pure ammonium sulfate. Crude ammonium sulfate containing considerable amounts of phenolic compounds and salts of pyridine was substituted for the pure salt in the titration represented by the third curve. Hardly a suggestion of an inflection remains, yet it will be shown that even in such unfavorable cases the end point may be located with a considerable degree of accuracy.

In the event that the titration curve is so flat as to render uncertain the location of the end point by direct observation, it has been customary to determine from the curve the change in potential, ΔE , for a given small change in the volume of the titrating solution, ΔV ; the maximum value of the ratio $\Delta E/\Delta V$ fixes the definitive value of V . $\Delta E/\Delta V$ is a sensitive function, however, and is considerably affected by even slight irregularities in E . It is therefore advisable to plot if the highest accuracy is desired. This process is

A SIMPLE MATHEMATICAL formula has been developed for determining the end point of a potentiometric titration. It is applicable only in cases in which the electron interchange between the electromotively active ions and the indicator electrode is the same on both sides of the end point, and it assumes that a cubic equation fits the titration data accurately near the point of equivalence. Its use reduces the necessary plotting to a minimum, thereby shortening the time required for an analysis. The formula has been applied to a specific titration selected from the group to which its use is theoretically least restricted—i. e., neutralization reactions. The results were found to compare very favorably in accuracy with the experimental data.

time-consuming and boresome. It is the object of this paper to point out an analytical solution applicable in many cases which permits of the determination of the end point directly from the titration curve by a simple calculation.

DEVELOPMENT OF FORMULA

The equation

$$E = E_0 - \frac{0.05915}{N} \log \frac{a_1}{a_2}$$

may be regarded as defining the potential of any indicator electrode at 25° C. a_1 and a_2 are the respective activities of the electromotively active substances. E_0 is a constant

fixed by the theoretical condition of unit values for both a_1 and a_2 , and N the number of Faradays passing. If the electronic transfer is such that the electrode reactions on both sides of the end point for a given titration involve the same value for N , it is evident that the curve E versus V is symmetrical with respect to the end-point inflection, since V , the volume of the titrating solution added, may be regarded as a measure of the ion activities concerned in the region of the equivalence point. Many of the most commonly employed oxidation and precipitation reactions and all neutralization titrations meet this requirement. It has been found in studying the curves for a large number of such titrations that a cubic equation fits the curve with sufficient accuracy over a fairly wide region on either side of the end point. The problem, therefore, resolves itself into a quest for a rapid method of locating the point of inflection of a cubic equation.

The type equation may be written

$$aV^3 + bV^2 + cV + d = E$$

By successive differentiation

$$d^2E/dV^2 = 6aV + 2b$$

Since the value of V at the end point must be such that the second derivative vanishes, it is not necessary to set up the complete equation to fix the inflection, as the determination of the constants a and b suffices.

If four equidistant points, V_1 , V_2 , V_3 , and V_4 , are selected from the portion of the titration curve covering the end point, and if k is the constant difference between them, and

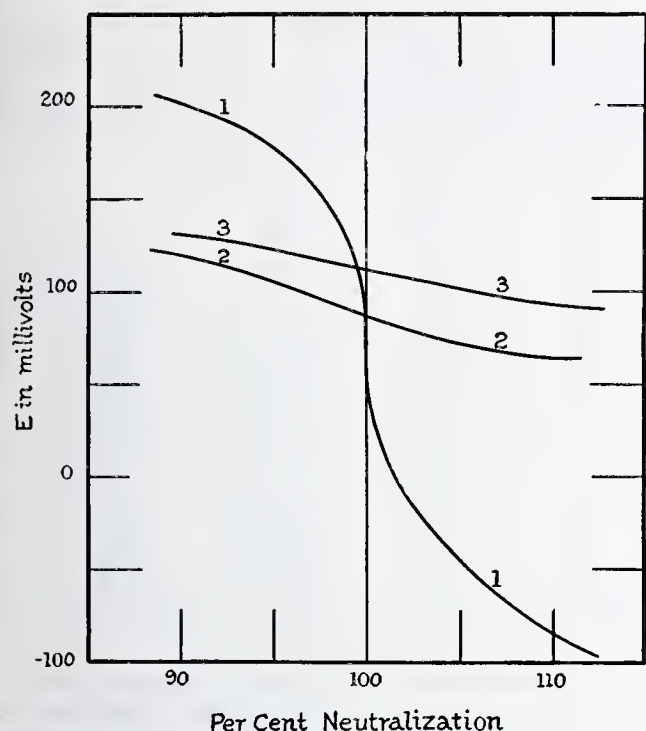


FIGURE 1

E_1 , E_2 , E_3 , and E_4 are the corresponding potential values, the following four simultaneous equations must be valid:

$$\begin{aligned} V_1^3 a + V_1^2 b + V_1 c + d &= E_1 \\ (V_1 + k)^3 a + (V_1 + k)^2 b + (V_1 + k)c + d &= E_2 \\ (V_1 + 2k)^3 a + (V_1 + 2k)^2 b + (V_1 + 2k)c + d &= E_3 \\ (V_1 + 3k)^3 a + (V_1 + 3k)^2 b + (V_1 + 3k)c + d &= E_4 \end{aligned}$$

From these equations it may be shown that

$$6a = \frac{D}{k^3}$$

and

$$2b = \frac{(kD' - V_2 D)}{k^3}$$

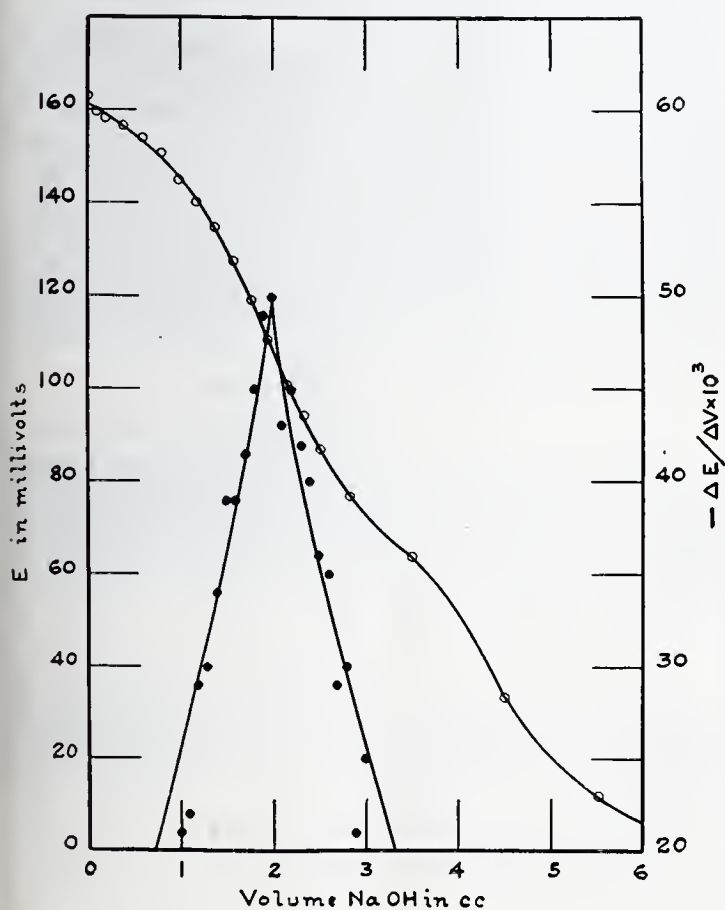


FIGURE 2

where D' is the first of the second tabular differences and D the third difference obtained by the successive subtraction of the four potentials. Substituting in the expression

$$d^2 E / dV^2 = 6aV + 2b = 0$$

the desired formula for V , the point of inflection, becomes

$$V = \frac{(V_2 D - k D')}{D} = V_2 - k \frac{D'}{D}$$

The accuracy in V is not limited to the accuracy with which the third tabular difference can be determined, as is evident from the last form in which the equation is written. The formula is precise, and the only assumption involved in its application is that the titration curve is accurately defined by a cubic equation over the region specified. The calculation for the inflection is a matter of a very few minutes.

TABLE I. TITRATION OF SULFURIC ACID IN PRESENCE OF CRUDE AMMONIUM SULFATE

EXPERIMENTAL DATA		INTERPOLATED DATA		$\Delta E / \Delta V \times 10^3$
NaOH Cc.	E Volts	NaOH Cc.	E Volts	
0.00	0.1635	0.9	0.1482	
0.10	0.1599	1.00	0.1461	21
0.20	0.1588	1.10	0.1439	22
0.40	0.1571	1.2	0.1410	29
0.60	0.1542	1.3	0.1380	30
0.80	0.1513	1.4	0.1346	34
1.00	0.1456	1.5	0.1307	39
1.18	0.1404	1.6	0.1268	39
1.38	0.1350	1.7	0.1225	43
1.58	0.1280	1.8	0.1180	45
1.77	0.1195	1.9	0.1132	48
1.95	0.1109	2.00	0.1082	50
2.15	0.1014	2.10	0.1039	43
2.34	0.0945	2.2	0.0994	45
2.52	0.0875	2.3	0.0952	42
2.82	0.0772	2.4	0.0912	40
3.50	0.0640	2.5	0.0876	36
4.50	0.0335	2.6	0.0841	35
5.50	0.0120	2.7	0.0812	29
		2.8	0.0782	30
		2.9	0.0760	22
		3.00	0.0735	25

End point (graphic method): 2.0 cc. NaOH
End point (analytic method): 1.955 cc. NaOH

APPLICATION OF FORMULA

Perhaps the most commonly encountered titrations presenting end points difficult to determine involve the neutralization of slightly acid but very concentrated salt solutions. For this reason the titration represented by Curve 3 of Figure 1 was selected to demonstrate the applicability of the proposed method. A small amount of sulfuric acid was added to a solution of 24.5 grams of crude ammonium sulfate, the concentration adjusted to about 1.5 M with respect to the salt, and the free acid neutralized with 0.1 N sodium hydroxide. The saturated quinhydrone electrode was used as the indicator electrode. All potentials were referred to a silver-silver chloride, 0.1 m potassium chloride electrode.

Figure 2 shows both the titration curve and its derivative. It will be observed that the slope of the E versus V curve decreases as the end point is passed and then increases again. This is due to at least two causes. The sulfuric acid is really titrated in a mixture of acids. Being by far the strongest acid present it is titrated first, but after it has been neutralized the effect of the reaction of the weakly acidic compounds pyridine sulfate and phenol with the base may be observed in the increased slope of the curve. Another factor in determining the course of the far end of the curve is the decomposition and oxidation of quinhydrone in alkaline solution. The measured potentials are much less certain as the solution becomes distinctly alkaline, and therefore the lower end of the curve is less accurately defined than the upper. The symmetry of the curve for this particular titration may thus be affected somewhat.

The first two columns of Table I contain the experimental data for Figure 2. The last three columns were obtained from a careful large-scale plot of these data. Application of the formula developed above to values selected from the third and fourth columns of the table results in the following:

VOLUMES	k	POTENTIALS	FIRST DIFF.	SECOND DIFF.	THIRD DIFF.
$V_1 = 0.9$		$E_1 = 0.1482$			
$V_2 = 1.6$	0.7	$E_2 = 0.1268$	-0.0214	-0.0102 = D'	
$V_3 = 2.3$	0.7	$E_3 = 0.0952$	-0.0316	+0.0099	+0.0201 = D
$V_4 = 3.0$	0.7	$E_4 = 0.0735$	-0.0217		

$$V = \frac{V_2 D - k D'}{D} = \frac{[1.6 \times (0.0201)] - [0.7 \times (-0.0102)]}{0.0201}$$

$$= \frac{0.03216 + 0.00714}{0.0201}$$

$$= 1.955 \text{ cc.}$$

Comparison of the analytically determined value for V , 1.955 cc., with the point of maximum rate of change of E with V as fixed by a carefully drawn plot of the derivative, 2.0 cc., shows that the difference is well within the accuracy of the titration.

A number of exactly similar titrations were made, differing only in the amount of acid added initially, and the end points determined by both methods. The results are listed in Table II. The analytic results were rounded to the nearest 0.1 cc. for computing the last column. The differences rarely exceed the probable error in drawing the $\Delta E/\Delta V$

versus V curve and are never greater than 0.2 cc. of 0.1 N solution.

TABLE II. COMPARISON OF GRAPHIC AND ANALYTIC METHODS FOR DETERMINING END POINT OF ELECTROMETRIC TITRATION

TITRATION	Graphic Cc.	VOLUME OF 0.1 N NaOH Analytic Cc.	Diff.
1a	7.6	7.671	-0.1
1b	7.6	7.647	0.0
2a	4.0	3.880	+0.0
2b	4.0	3.867	+0.1
3a	4.6	4.617	0.0
3b	4.7	4.752	-0.1
3c	4.65	4.593	+0.06
3d ^a	4.7	4.545	+0.2
		4.775	-0.1
4	1.25	1.181	+0.07
5	7.7	7.576	+0.1
6	11.3	11.394	-0.1
7a	2.0	1.955	0.0
7b	2.1	1.923	+0.2
8a	0.8	0.705	+0.1
8b	0.8	0.722	+0.1
9a	3.9	3.930	0.0
9b	3.9	3.938	0.0

^a Titration curve visibly unsymmetrical so that two sets of points were selected for analytic solution.

If the indicator electrode is highly reversible, as is the quinhydrone electrode except in appreciably alkaline solution, and comes quickly to equilibrium with the solution, by exerting some care in making the titration the four necessary equidistant points may be obtained directly without recourse to any plotting. In this case it is safest to calculate from at least two sets of points.

RECEIVED August 4, 1931.

A New Microanalytical Test for Carbon Disulfide

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A REVIEW of the literature shows only three tests for carbon disulfide sufficiently sensitive to be considered microanalytical tests: Feigl and Weisselberg's (3) tests with Hector's base and nickel acetate and with formaldehyde and plumbate; Feigl and Chargaff's (2) iodine azide test. These tests, however, present certain disadvantages. Hector's base is not readily available; the formaldehyde-plumbate test requires undue precautions of procedure; sodium azide is extremely explosive; and the test itself is not sufficiently rapid.

A new microanalytical test, based on the formation of the brown copper salt of diethyldithiocarbamic acid from carbon disulfide, diethylamine, and copper acetate, suggested itself to the writer on noting a brief resumé (4) of Mayer and Fehلمان's patented method of precipitating carbon disulfide from gas by absorption with a mixture of amines and metallic oxides (5), and on recalling Callan and Henderson's recent use of diethyldithiocarbamic alkaline salts as microcolorimetric reagents for copper (1). The reagents used are as follows: 1% (by volume) diethylamine in absolute alcohol; 0.05% (by weight) copper acetate c. p. in absolute alcohol.

To test for the presence of carbon disulfide, 1 cc. of diethylamine solution and 5 drops of copper acetate solution are added to 1 cc. of the solution to be tested. Colorless solutions in acetone, chloroform, ether, and alcohol give a golden-yellow color at a carbon disulfide concentration of 1 to 100,000, a pronounced yellow at 1 to 500,000, and a faint but perceptible tinge at 1 to 1,000,000. In aqueous solutions, a precipitate is formed, but the sensitiveness is the same.

Dimethylsulfide and ethyl mercaptan, pure and 1 to 100, failed to give the reaction. However, pure thioacetic acid gave a similar reaction to carbon disulfide, and it is suggested

that the test is possibly applicable to double-bonded sulfur compounds generally.

A series of colorimetric standard concentrations of chemically pure carbon disulfide precipitated by equivalent amounts of the reagents has been prepared wherever quantitative determinations of traces of carbon disulfide in solution were made, but it is undoubtedly possible to make more exact quantitative measurements by the use of a colorimeter.

The writer has applied this microanalytical test to toxicological studies, and has found it well suited to them; a few drops (as little as 0.1 cc.) of insect blood showed the presence of carbon disulfide when the insects were exposed to saturated vapors of the fumigant for 2 minutes.

ACKNOWLEDGMENT

Grateful acknowledgment is made to Dr. Ralph M. Hixon and to Dr. Charles H. Richardson who offered helpful suggestions and criticisms, and to Rohm & Haas Company for a fellowship grant for the physiological investigation of the insecticidal toxicity of carbon disulfide.

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RECEIVED June 12, 1931.

Titration of Zinc with Potassium Ferrocyanide

Use of Diphenylamine or Diphenylbenzidine as Internal Indicators

I. M. KOLTHOFF AND E. A. PEARSON, *University of Minnesota, Minneapolis, Minn.*

THE general application of the well-known zinc titration with potassium ferrocyanide as a reagent has increased considerably since Cone and Cady (2) proposed the use of diphenylbenzidine as an internal indicator. Diphenylamine may also be used, but it has the slight disadvantage that the amount of indicator affects the results. In testing Cone and Cady's procedure, Kolthoff (3) found that different factors, such as the acidity, kind of acid present, concentration of zinc, presence of neutral salts, speed of and temperature during the titration and ferricyanide content of the reagent, affect the location of the end point. Kolthoff used diphenylamine as an indicator and recommended that the titration be performed at a temperature of around 50° C. Under these conditions a fairly rapid direct titration to the end point can be made and a back titration of the excess ferrocyanide with a zinc solution of known content is not necessary. For the determination of small amounts of zinc, Bradley (1) recommends titrating the solution after acidifying with hydrochloric acid and the addition of 4 to 6 drops of an aqueous solution of 20 per cent potassium ferricyanide at a temperature of 60° to 70° C. In a study on the co-precipitation of zinc sulfide with copper sulfide the authors had to determine the zinc content of solutions under varying conditions, and it appeared necessary to make a systematic investigation on the influence of different factors upon the titration in order to find a uniform procedure applicable to varying conditions. An outline of the more than 1000 titrations which have been made will be given in this account.

EXPERIMENTAL PROCEDURE

MATERIALS. Zinc sulfate (c. p.) of different origin was recrystallized two to three times from water and dried in desiccators at the proper vapor tension (relative water v. t., 0.65 to 0.70), until constant weight was obtained. The salt was analyzed and shown to have the composition $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Moreover, solutions of spectroscopically pure zinc (kindly supplied by New Jersey Zinc Company) in dilute sulfuric acid were prepared. It may be mentioned that solutions of Kahlbaum's zinc were also made, but this zinc is not so pure as the product of the New Jersey Zinc Company, and leaves, after dissolving the metal in dilute sulfuric acid, a black, spongy residue.

Samples of c. p. potassium ferrocyanide were recrystallized from water twice and dried in a desiccator over deliquescent sodium bromide until constant weight was obtained. A water determination showed the composition $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ (drying at 110° C.).

THE METHOD of the titration of zinc with potassium ferrocyanide using diphenylamine or diphenylbenzidine as an indicator has been submitted to a systematic examination. The results obtained are mainly dependent upon the conditions of titration (speed of adding ferrocyanide, temperature, direct or back titration); the most favorable acidity and concentration of ammonium sulfate being 0.5 to 1.5 N and at least 1 to 2 per cent are of minor importance. In agreement with Cone and Cady, it was found that with the use of diphenylbenzidine no indicator correction has to be applied, whereas with the use of 1 per cent diphenylamine 0.033 cc. of 0.025 M ferrocyanide has to be added as a correction per 1 drop of indicator (0.023 ml.) to the final titration figure. The authors prefer the use of diphenylamine to diphenylbenzidine, as the latter sometimes gives much less pronounced color changes.

Commercial and c. p. potassium ferricyanide salts were recrystallized from water and dried in the air.

Ammonium sulfate and other salts, c. p., were recrystallized once or more from water.

STANDARD SOLUTIONS. Zinc sulfate, 0.05 M (if the strength was somewhat different, the figures were recalculated in order to relate them to the strength of the standard solution), and 0.025 M potassium ferrocyanide (10.5580 grams of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ per liter), containing 0.15 gram of $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.2 gram of sodium carbonate per liter, the latter added in order to stabilize the solution, were used. In the final experiments the addition of ferricyanide to the standard solution was omitted. According to the equation



theoretically, 25 cc. of the zinc solution requires 33.33 cc. of the ferrocyanide solution. A 1 per cent solution of diphenylamine or diphenylbenzidine in concentrated sulfuric acid (indicated by D. A. or D. B.) was used as indicator.

RESULTS OF TITRATIONS (4)

If the reagent is added too rapidly, the equivalence point is easily passed. Large amounts of ammonium sulfate have a pronounced retarding effect, as may be inferred from the results in Table I. In each case the titration was carried out rapidly until near the end point where the reagent was added drop by drop. After the end point had been reached, the yellowish green suspension was titrated back slowly with zinc solution, and a sharp color change to purple-blue was observed. In all cases a correction of 0.033 cc. of 0.025 M ferrocyanide for each drop of diphenylamine was added to the titration figure.

The experiments reported in Table II were carried out in such a way that the reagent was added slowly to within 2 ml. from the theoretical end point, and then drop by drop until the color changed to yellowish green (false end point). After waiting then for 2 to 3 minutes, a characteristic purple color developed, whereupon the titration could be finished by dropwise titration to the definite end point. As the result of a large number of experiments, it can be definitely stated that the speed of titration is of great influence only near the equivalence point. In order to obtain reproducible results, careful dropwise titration must be made to the appearance of the false end point, and after waiting for the appearance of the blue or purple color the titration is finished by slow dropwise titration to the final end point. The appearance of the false end point is very characteristic.

The light blue solution fades out to a pale green or almost colorless solution which gradually becomes purple. The longer the period of standing the more brilliant becomes the purple color. The solution should be vigorously stirred or shaken during the entire titration and especially while waiting for the purple color to develop. If the titration is carried out too rapidly near the end point, the false end point, which develops 0.2 to 0.4 cc. short of the true end point, will be missed and high results will be obtained (as shown in Table I).

TABLE I. EFFECT OF RAPID TITRATION AND DIFFERENT AMOUNTS OF AMMONIUM SULFATE
(25 cc. of 0.05 M ZnSO₄; 10 cc. of 4 N H₂SO₄; and 2 drops of D. A., temp., 24° C.)

(NH ₄) ₂ SO ₄ Added Grams	DIRECT TITRATION	DEVN. FROM THEORY %	BACK TITRATION	DEVN. FROM THEORY %
0.5	33.11	-0.7	33.08	-0.8
1.0	33.24	-0.3	33.21	-0.4
1.0	33.27	-0.2	33.21	-0.4
5.0	34.67	+4.0	33.47	+0.4
5.0	34.77	+4.3	33.41	+0.2

TABLE II. VERY SLOW TITRATION
(Presence of ammonium sulfate; other conditions as described in Table I)

(NH ₄) ₂ SO ₄ Grams	DIRECT TITRATION	DEVN. FROM THEORY %
1	33.04	-0.9
1	33.03	-0.9
8	33.13	-0.6
8	33.14	-0.6

If the titration is carried out very slowly under these conditions, even very large quantities of ammonium sulfate only slightly affect the location of the permanent end point. The results given in Table III show that within wide limits, the concentration of sulfuric acid and of ammonium sulfate and the dilution are without influence upon the results. Large amounts of ammonium sulfate seem to bleach the color to some extent, possibly because the salt decreases the hydrogen-ion concentration and consequently the oxidation potential of the ferri-ferrocyanide solution. In all the titrations, the ferrocyanide was added fairly rapidly under thorough shaking of the titration flask to about 1 cc. from the theoretical end point, and from there on slowly. After development of the purple color the reagent was added very slowly, drop by drop, until the permanent color change was reached. Especially at high acidity (about 1 to 2 N) very sharp color changes were observed. The results are reproducible within about 0.5 per cent or closer. The speed of titration, even when the reagent is added drop by drop, has an appreciable influence in the direct titration, especially near the end point. de Koninck and Prost (7) assume that the zinc ferrocyanide first formed is slowly transformed into the potassium zinc ferrocyanide. However, as many other authors notice, on standing, near the end point the appearance of the precipitate seems to change entirely. At the false end point the ferrocyanide concentration is large enough to decrease the oxidation potential to such an extent that the quinoid form of the indicator is reduced to the colorless form. On standing, the ferrocyanide concentration decreases, owing to the transformation of the precipitate into the stable and less soluble double salt, the oxidation potential increases, and the indicator is oxidized again. Kolthoff and Verzyl (6) have studied this change of the oxidation potential near the equivalence point. The direct titration at room temperature, although it yields reproducible results, is not recommended for routine work, as the manipulations require much attention and time. The results obtained are about 0.6 to 1 per cent low. If, after such a slow titration, an excess of reagent (5 to 25 per cent) is added which is titrated back with standard zinc solution, the results are raised only 0.3 to 0.4 per cent.

TABLE III. TITRATION OF ZINC SULFATE WITH POTASSIUM FERROCYANIDE

(25 cc. of 0.05 M ZnSO₄; 0.025 M K₄Fe(CN)₆ containing 0.15 gram of K₄Fe(CN)₆ per liter; and 6 drops of D. A. corrected for indicator; temp., 20° C.)

4 N H ₂ SO ₄	(NH ₄) ₂ SO ₄	WATER ADDED	FERRO- CYANIDE USED	DEVN. FROM THEORY	COMMENT ON END POINT
Cc.	Grams	Cc.	Cc.	%	
10	1	90	33.01	-1.0	Fairly good
10	2	90	33.08	-0.7	Fairly good
10	2	150	33.09	-0.7	Fairly good
10	4	90	33.09	-0.7	Fairly good
10	8	90	33.22	-0.4	Fairly good
20	1	90	32.97	-1.1	Fairly good
20	2	90	33.11	-0.7	Good
20	4	90	33.15	-0.6	Very good
20	8	90	33.24	-0.3	Good
30	1	90	32.97	-1.1	Good
30	2	90	33.06	-0.8	Very good
30	2	150	33.06	-0.8	Very good
30	4	90	33.19	-0.4	Very good
30	8	90	33.28	-0.2	Good
50	1	90	33.05	-0.8	Very good
50	2	90	33.08	-0.7	Very good
50	2	150	33.04	-0.8	Very good
50	4	90	33.15	-0.6	Very good
50	8	50	33.26	-0.2	Very good
50	8	90	33.34	0.0	Very good
50	8	200	33.37	+0.1	Very good

BACK TITRATION AT ROOM TEMPERATURE

The procedure is more satisfactory if the reagent is added fairly rapidly until an excess of 5 to 15 per cent is present. The mixture in the flask has a creamy light yellowish green color. By back titration with standard zinc solution, a change to purple is obtained at the end point which coincides within 0.3 per cent with the equivalence point. Here the change from purple to yellowish green is completely reversible and most data are based on the latter end point. Some results, reproducible within 0.2 per cent, are given in Tables IV and V.

TABLE IV. RESULTS OF BACK TITRATION
(25 cc. of 0.05 M ZnSO₄; 10 cc. of water; 10 cc. of 4 N H₂SO₄; 1 gram of (NH₄)₂SO₄; 2 drops of 1% D. A.; temp., 24° C.)

EXCESS REAGENT ADDED ^a	BACK TITRATION	DEVN. FROM THEORY
Cc.		%
1.0	33.30	-0.1
1.0	33.35	+0.1
2.0	33.35	+0.1
2.0	33.35	+0.1
5.0	33.40	+0.2
5.0	33.38	+0.2

^a Added fairly rapidly (70 to 90 seconds). Near the end point the speed of addition of ferrocyanide was decreased.

TABLE V. RESULTS OF FURTHER BACK TITRATIONS
(25 cc. of 0.05 M ZnSO₄; 90 cc. of water; 30 cc. of 4 N H₂SO₄; 2 grams of (NH₄)₂SO₄; 6 drops of 1% D. A.; temp., 24° C.)

EXCESS REAGENT ADDED	BACK TITRATION	DEVN. FROM THEORY
Cc.		%
0.2	33.32	0.0
1.0	33.32	0.0
1.0	33.34	0.0
2.0	33.37	+0.1
5.0	33.36	+0.1

If the direct titration method was applied (slow titration and waiting for the appearance of the false end point), the results again were 0.9 to 1.1 per cent low. In agreement with Cone and Cady (2), it was found that with diphenylbenzidine the amount of indicator is without influence upon the results, whereas increasing the concentrations of diphenylamine lowers the titration figures. Nevertheless, in most of the experiments diphenylamine was used because under some conditions a less sharp color change was observed with diphenylbenzidine (5). Each drop (0.023 cc.) of 1 per cent diphenylamine lowers the result by 0.033 cc. of 0.025 M ferrocyanide (Table VI). If necessary a correction may be applied for the indicator effect. The use of 2 drops of 1 per cent diphenylamine will do for a volume of 50 cc., and for a larger volume a correspondingly larger quantity of indicator is used. Many of the experi-

ments reported in Tables I to V were repeated with diphenylbenzidine as an indicator and the same phenomena were observed as with diphenylamine.

TABLE VI. EFFECT OF DIFFERENT AMOUNTS OF DIPHENYLBENZIDINE AND DIPHENYLAMINE

(25 cc. of 0.05 *M* ZnSO₄; 10 cc. of water; 1 gram of (NH₄)₂SO₄; 10 cc. of 4 *N* H₂SO₄ + 2 drops of 1% ferricyanide; temp., 24° C.; back titration; 1 drop of 1% indicator = 0.023 cc.)

1% INDICATOR Drops	FERRICYANIDE TAKEN Cc.	DEVN. FROM THEORY %
DIPHENYL BENZIDINE		
2	33.44	+0.3
4	33.40	+0.2
8	33.44	+0.3
12	33.44	+0.3
DIPHENYLAMINE		
2	33.37	+0.1
4	33.31	-0.1
8	33.15	-0.5
12	33.04	-0.9

INFLUENCE OF CONCENTRATION OF FERRICYANIDE ON TITRATIONS AT ROOM TEMPERATURE

From the results of experiments described in Tables I to VI, it is concluded that at room temperature the direct titration to the end point is quite a tedious procedure. If only very small amounts of zinc are present in the solution, it is extremely hard to obtain accurate and concordant results according to this method, whereas a sharp end point is observed if an excess of reagent is added which is titrated back with standardized zinc solution.

The standard ferrocyanide solution used in the titrations contained only 0.15 gram of potassium ferricyanide per liter. In the determination of small amounts of zinc, the ferricyanide content of the mixture during the titration is so small that no distinct blue color is developed. Therefore, it is necessary to add some ferricyanide to the solution. Too large amounts should be avoided, as seriously low results are obtained. The oxidation potential is increased too much, and therefore the color change may take place before the equivalence point has been reached. Moreover, it is possible that part of the ferricyanide oxidizes the indicator in an irreversible way, whereby the ferricyanide is reduced to ferrocyanide.

A large number of titrations, in which the concentration of sulfuric acid, ammonium sulfate, and ferricyanide was varied within wide limits, were performed in order to arrive at a procedure which would hold for the titration of different amounts of zinc. It was found that the acidity and the ammonium sulfate concentration are of minor importance, whereas the addition of 1 to 4 drops of a 1 per cent solution of potassium ferricyanide is the most favorable amount, larger quantities being harmful especially at low zinc concentrations. With very large amounts of ferricyanide (1 cc. of 10 per cent solution or more) the solution does not turn purple at all, but dirty green, and the end point is marked by a change from dark to bright green (with diphenylamine as indicator). The amount of ferricyanide Bradley (1) recommended, 2 to 3 drops of 20 per cent K₃Fe(CN)₆, is undoubtedly too large, especially when the titration is performed at 60° to 70° C., as Bradley suggests. It should be mentioned here that a ferricyanide solution is not very stable. It has to be prepared in water of good quality, the addition of a trace of (0.03 per cent) sodium carbonate having a stabilizing effect. It is also best to prepare a fresh solution every 4 or 5 days and to keep it protected from the action of sunlight. No special study has been made of the stability of ferricyanide solutions.

In the titration of very small amounts of zinc, the use of diphenylbenzidine has advantages over diphenylamine,

since no correction has to be applied for the oxidation of the indicator. In most of the experiments 2 drops of 1 per cent diphenylamine were used and, in this case, a correction of 0.066 cc. of 0.025 *M* ferrocyanide had to be added to the titration figure in order to account for the indicator effect. This was done in all experiments listed in this paper.

The following procedure is shown to give satisfactory results for the titration of 3 mg. or larger quantities of zinc. To a measured volume of the 0.05 *M* zinc solution, 10 cc. of water, 10 cc. of 4 *N* sulfuric acid, 1 gram of ammonium sulfate, 2 drops of 1 per cent potassium ferricyanide, and 2 drops of 1 per cent diphenylamine are added, whereupon the reagent is added fairly rapidly until a distinct excess is present. The ferrocyanide is titrated back with a standard zinc solution, the end point being marked by a sharp color change from yellowish green to purple. In the titration of very small amounts of zinc the use of a microburet is recommended.

In Table VII some of the results are recorded.¹ The third and fourth columns give the figures without correcting for the indicator effect, the fifth and sixth after correction. With 2 drops of 1 per cent diphenylbenzidine, about the same results are obtained as given in the fifth and sixth columns. As a whole, the procedure gives satisfactory results for amounts of zinc varying within wide limits. In the application of the method, standardization of the ferrocyanide solution against a zinc solution of known content under the same conditions used in the titration is recommended. As 2 drops of ferricyanide are added separately to the solution, it is not necessary to add it to the standard ferrocyanide solution.

TABLE VII. TITRATION OF VARYING AMOUNTS OF ZINC AT ROOM TEMPERATURE (22° C.)

0.05 <i>M</i> ZINC TAKEN Cc.	(Diphenylamine as indicator)					
	EXCESS FERRI- CYANIDE ADDED %	NOT COR. FOR INDICATOR		COR. FOR INDICATOR		PERFORMANCE OF TITRATION
		Zinc found Cc.	Devn. from theory %	Zinc found Cc.	Devn. from theory %	
1.90	50	1.88	-1.0	1.92	+1.0	Slow
3.68	30	3.60	-2.2	3.64	-1.1	Slow
4.30	20	4.28	-0.5	4.32	+0.5	Slow
4.50	40	4.48	-0.5	4.52	+0.5	Slow
9.96	0.7	9.90	-1.3	9.94	-0.2	Slow
10.20	10	10.10	-1.0	10.14	-0.6	Slow
15.06	3.3	15.07	0.0	15.11	+0.3	Rapid
15.20	10	15.10	-0.7	15.14	-0.4	Slow
19.95	1.6	19.81	-0.7	19.85	-0.7	Slow
25.00	0	24.72	-1.1	24.76	-0.9	Very slow; direct
25.00	3	24.85	-0.6	24.89	-0.4	Slow
25.00	3	25.00	0.0	25.04	+0.15	Rapid
25.00	6	25.02	+0.1	25.06	+0.25	Rapid
25.00	5	24.77	-0.9	24.83	-0.7	No (NH ₄) ₂ SO ₄ added; rapid

TITRATION AT HIGHER TEMPERATURE

Kolthoff (3) previously pointed out some of the difficulties met with in the direct titration of zinc at room temperature. He recommended titration at 50° to 60° C. and observed a false end point before the definite color change was obtained. About 0.5 cc. before the final end point the dark blue color goes suddenly over to yellowish green. If one waits 15 to 30 seconds, the change reverses itself and the liquid takes on a characteristic bright blue-violet color. The titration is continued drop by drop until the color no longer turns back to blue-violet after 20 seconds. The color change is not so brilliant as at room temperature, but, on the other hand, the titration can be carried out at 50° to 60° C. much more quickly than at room temperature and the results are quite reproducible.

The authors could confirm these statements if the indi-

¹ The experimental conditions are described more fully in the thesis of E. A. Pearson (Minnesota, 1931).

cator and 2 to 4 drops of 1 per cent potassium ferricyanide were added after heating the solution and just before the titration was started. The method was tested under different conditions at 50° to 60° C., and it was found that the same procedure can be followed as given for the experiments in Table VII. Again, a large excess of ferricyanide is harmful. Especially for the determination of small quantities of zinc (25 mg. or less), the titration in warm solution is advantageous. In the latter case it is well to add a small excess of ferrocyanide followed by back titration, since the direct titration takes time. Some of the results are reported in Table VIII. The experiments were made under the same conditions as described for those in Table VII.

TABLE VIII. TITRATION OF VARYING AMOUNTS OF ZINC AT 50° TO 60° C.

(Ferri-cyanide and indicator added after heating solution and immediately before addition of ferrocyanide)

EXCESS 0.025 M FERRO- CYANIDE TAKEN Cc.		NOT COR. FOR INDICATOR Zinc found Cc.		COR. FOR INDICATOR Zinc found Cc.		PERFORMANCE OF TITRATION
0.05 M FERRO- CYANIDE ADDED %		Devn. from theory %		Devn. from theory %		
0.99	23	0.99	0.0	1.03	+4	Slow
3.50	10	3.45	-1.4	3.48	-0.6	Slow
5.02	7	4.90	-2.4	4.94	-1.6	Slow
10.14	7	10.18	+0.3	10.22	+0.8	Fairly rapid
15.04	0	14.91	-0.9	14.95	-0.6	Direct; after de- velopment of color at false end point, pro- ceeded slowly
15.00	2.7	14.91	-0.6	14.95	-0.3	Rapid
20.03	5	19.88	-0.7	19.92	-0.5	Slow
25.00	0	24.72	-1.1	24.76	-1.0	Direct
25.00	0	24.74	-1.0	24.78	-0.9	Direct
25.00	7.5	24.74	-1.0	24.78	-0.9	Rapid
25.00	12.8	24.90	-0.4	24.94	-0.2	Very rapid

INFLUENCE OF ADDITION OF OTHER SUBSTANCES

Hydrochloric acid has no interfering effect. It can be used instead of sulfuric acid if the solution contains at least 0.5 to 1 gram of ammonium sulfate. The most favorable acidity is again 0.5 to 1 *N*.

Ammonium chloride, if present in large amounts, retards the development of the color change as ammonium sulfate does. It has practically no influence upon the results, yielding about 0.2 per cent lower results than ammonium sulfate.

Sodium sulfate is without any influence, at least if ammonium sulfate is present.

Earth alkali salts in small quantities (less than 0.5 gram) in the presence of ammonium sulfate do not exert any influence; if present in larger amounts they have a tendency to lower the results. The interference, however, is not serious.

Ferric iron and other cations which form insoluble ferrocyanides interfere very strongly and have to be removed. Kolthoff and Verzyl (6), in their potentiometric work, used fluorides to render ferric iron harmless. This substance was used in this work also. The stability of the ferric fluoride complex decreases with increasing acidity, and therefore it is necessary to regulate the acidity very carefully. At too low acidity the oxidation potential is not high enough to produce the oxidation of the indicator. The following method, though not very practical, could be used for the titration of 30 mg. of zinc in the presence of less than 20 mg. of ferric iron:

Ten cubic centimeters of 0.05 *M* zinc sulfate were treated with 7 grams of potassium fluoride, 50 to 60 cc. of 48 per cent hydrofluoric acid solution, and about 50 cc. of water. The mixture was heated to 60° to 70° C., 2 drops of 1 per cent ferricyanide and 4 to 6 drops of diphenylamine were added, and the titration started. The color change was not so sharp as under ordinary conditions (reproducibility 1 per cent).

Aluminum. The potentiometric method gives no end point in the presence of even traces of aluminum salts. With the indicator method, 0.5 gram of aluminum chloride or less had practically no effect (results were raised about 0.5 per cent); with much larger amounts of aluminum salts no end point could be detected.

DISCUSSION OF DIRECT TITRATION

END POINT AT ROOM TEMPERATURE. The reagent can be added fairly rapidly until about 1 cc. before the equivalence point. Upon further careful addition of reagent, a false end point is found (from purplish blue to yellowish green). If one waits 1 to 2 minutes, a characteristic blue-violet color develops; the titration is continued; the reagent is added drop by drop with continuous shaking of the titration flask until the permanent end point is reached. This procedure cannot be recommended for general use, as the method is time-consuming and the false end point may be passed if the addition of reagent is not regulated very carefully.

END POINT AT 50° TO 60° C. The titration can be carried out under usual conditions until the color changes from purplish blue to yellowish green (false end point). After waiting for 15 to 30 seconds, the characteristic bluish color develops and the titration can be finished. The end point is reached when the blue color does not come back after 20 seconds' waiting. The procedure can be used for the titration of 25 mg. of zinc, or larger quantities. For the determination of quantities smaller than 25 mg., the back titration method at room temperature or at 50° to 60° C. is recommended.

General Procedure. Add to a measured volume of the zinc solution 1 gram of ammonium sulfate, sufficient sulfuric acid to make the acidity about 1 *N*, 2 drops of 1 per cent potassium ferricyanide, and 2 drops of 1 per cent diphenylamine (or 1 per cent diphenylbenzidine). If the titration is carried out at 50° to 60° C., the ferricyanide and indicator are added after heating the solution and immediately before adding the reagent. The ferrocyanide solution is added with normal speed until an excess is present. During the addition of the reagent the titration flask is continuously shaken. After 1 to 2 minutes' waiting, the excess of reagent is titrated back with a standard zinc solution; the end point is reached when the color changes from yellowish green to a characteristic blue-violet. The color change is very sharp (to 1 drop of 0.025 *M* ferrocyanide). If diphenylamine is used as an indicator, 0.07 cc. is added as a correction to the consumed volume of 0.025 *M* ferrocyanide.

One cubic centimeter of 0.025 *M* ferrocyanide corresponds to 2.45 mg. of zinc. At room temperature approximately theoretical results are found; at 50° to 60° C. they run about 0.5 to 1 per cent low. If quantities of zinc smaller than 20 mg. have to be titrated, it is recommended to add the ferrocyanide slowly. Small amounts of alkali and earth alkali salts and aluminum do not influence the results. Ferric iron interferes, but amounts smaller than 20 mg. can be made harmless by titrating at 60° to 70° C. in a solution containing a large quantity of potassium fluoride and hydrofluoric acid.

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Direct Electrometric Titration of Certain Coal-Tar Food Dyes

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THE titration of dyes with titanium trichloride as originally formulated by Knecht and Hibbert (8) has found wide application, and is the usual method now employed for the evaluation of many dye-stuffs. The end point in their method is indicated by the disappearance of the color, but in some cases the change is not sharp or is masked by the color of the reaction products. This has led investigators to seek a more precise method of determining the end point, and since the reaction involved is one of oxidation-reduction, electrometric methods were indicated.

Jones and Lee (7) have described an electrometric method for the titration of azo dyes, and Kolthoff and Robinson (11) have also presented a somewhat similar method for the estimation of "nitro bodies." In both of these investigations, the indirect method was used—i. e., an excess of standard titanium trichloride was added, and after the reduction was complete, a back titration with standard ferric alum solution was made, using an electrometric method to determine the end point.

Kolthoff and Furman (10) mention that Kolthoff and Tomicek (unpublished studies) found the direct electrometric titration of methylene blue to be possible in the presence of Rochelle salt. Kolthoff and Robinson (11) also attempted a direct titration of "nitro bodies," but decided that under their conditions, the reaction, although giving results (which they did not publish), was too slow to be of practical use. The authors have found that a direct potentiometric titration of certain coal-tar food dyes can be made satisfactorily if a suitable buffer-catalyst is present. The term "buffer-catalyst" as used in this paper applies to the salt which is added to the reaction flask before each titration. The function of this salt is to regulate the hydrogen-ion concentration, while at the same time it also appears to exert a specific promoting effect on the reduction.

PROCEDURE

APPARATUS. The electrical apparatus used was as follows: A Leeds and Northrup type K potentiometer, an Eppley standard cell, a portable d'Arsonval type galvanometer, a storage battery, a calomel half-cell, and a platinum-wire electrode. The arrangement of apparatus as given by Jones and Lee (7) was found to be satisfactory for the purpose, the only modification being the addition of a mechanical stirrer to ensure a more effective agitation of the liquid in the titration flask. Hostetter and Roberts (6) have given instructions in regard to the care of the platinum electrode, which were found to be very helpful. Clark (2) has described an electrode vessel which relieves the congestion of apparatus noticeable at that point.

MATERIALS. The dyes used were commercial, certified

A METHOD of making a direct electrometric titration of certain coal-tar food dyes belonging to the azo, triphenylmethane, nitro, and pyrazolone groups, respectively, is given. A buffer salt, usually sodium bitartrate or sodium citrate, is present in each case. Low results obtained for some dyes with sodium bitartrate are attributed to its reducing action on the dye. A number of typical titration curves are presented.

An attempt was made to estimate mixtures of the above dyes from the form of the titration curve with success in one case only. However, with two dyes which differ sufficiently in their oxidation potential it is believed that a successful titration can be made.

food colors from several manufacturers. The buffer salts were of C. P. or U. S. P. quality. The titanous chloride solution was made up approximately 0.05 N and standardized as described in the U. S. Department of Agriculture Bulletin 1390 (1). LaMotte's 20 per cent titanium trichloride was used. Kolthoff and Tomicek (12) have also given a very satisfactory and complete discussion on the purity, preparation, and standardization of titanium trichloride solutions for potentiometric titrations.

DETERMINATION. The percentage of pure coal-tar dye in a sample was first determined in the usual manner using standard titanium trichloride solution and a buffer which is known (5) to give accurate results with the dye under question. From these values aqueous solutions were made containing exactly 1 gram of pure dye per 100 cc. of solution. From this solution of known concentration, aliquot portions were pipetted into the titration flask, the volume of solution adjusted to approximately 100 cc., the mixture heated to boiling, and titrated, under an atmosphere of carbon dioxide, in the usual electrometric manner, noting the voltage after each addition of reducing solution. Heat was applied to keep the mixture between 90° and 100° C. throughout the titration. It was found in some cases, especially with the triphenylmethane dyes, that the voltage did not become constant for several minutes, but in general the reading could be taken as soon as the potentiometer had been adjusted.

RESULTS

The dyes that were titrated electrometrically with satisfactory results are given in Table I, which also shows the class to which the dye belongs and the buffer used in each case.

TABLE I. DYES EVALUATED BY ELECTROMETRIC TITRATION

NAME OF DYE	COLOR INDEX No.	CLASSIFICATION	BUFFER
Amaranth	184	Monazo	Sodium citrate
Orange	150	Monazo	Sodium bitartrate; sodium citrate; sodium bicarbonate
Ponceau 3R	80	Monazo	Sodium citrate
Ponceau SX	"	Monazo	Sodium bitartrate
Sunset Yellow FCF	"	Monazo	Sodium citrate
Brilliant Blue FCF	"	Triphenylmethane	Sodium bitartrate
Light Green SF Yellowish	670	Triphenylmethane	Sodium bitartrate
Guinea Green B	666	Triphenylmethane	Sodium bitartrate
Fast Green FCF	"	Triphenylmethane	Sodium bitartrate
Naphthol Yellow S	10	Nitro	Sodium bitartrate
Tartrazine	640	Pyrazolone	Sodium bitartrate

" Identity may be established by consulting reference (1).

Curve 2, Figure 1, is a typical curve obtained when Amaranth was titrated using sodium citrate as a buffer. The short line crossing the curve at 16.55 cc. indicates the point at which the color disappeared and would be considered the end

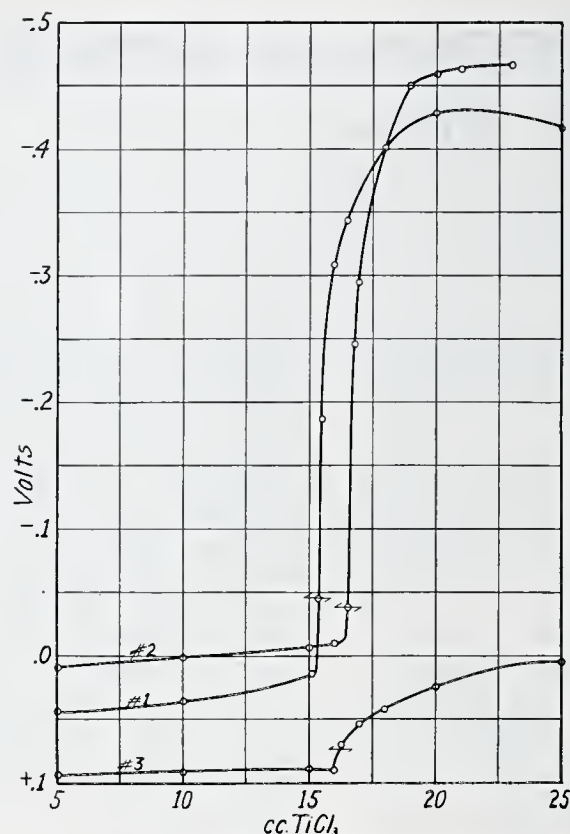


FIGURE 1. ELECTROMETRIC-TITRATION CURVES FOR AMARANTH USING THREE DIFFERENT BUFFERS. Curve 1, 0.1 gram + 5 grams of sodium bitartrate; curve 2, 0.1 gram + 5 grams of sodium citrate; curve 3, 0.1 gram + 1.5 cc. concd. HCl

point when titrating in the usual manner. Very close to the same values should be assigned as the end point from an inspection of the curve. Curve 1, Figure 1, shows the result when sodium bitartrate is used as a buffer. The end point is at 15.40 cc. and is all that could be desired for sharpness, but 1.15 cc. less of standard solution has been consumed to reduce the same quantity of Amaranth. This result further confirms, by a new method, the report (4) that low results are obtained when sodium bitartrate is used as a buffer for Amaranth. The short lines crossing these as well as the other curves presented in this paper indicate the end point as observed by the color changes.

It has also been reported (4, 5) that low results are obtained under similar conditions with Ponceau 3R and Sunset Yellow FCF. The electrometric-titration curves on these two dyes again confirm the previous reports and are very similar to the Amaranth curves presented. No explanation has previously been given as to why the bitartrate should give a low result, it being merely stated and demonstrated that such was the case. It seems reasonable to assume that these low results are due to a reducing action of the bitartrate upon the dye. It is well known that in some cases tartrates act as reducing agents, and it has been found by the senior author (unpublished investigation) that sodium bitartrate will decolorize sodium indigo disulfonate, whereas sodium citrate under the same conditions has no effect. It is also worthy of note that the dyes which give low results, in general, are also very easily reduced. From a consideration of this indirect evidence coupled with the direct observation that a portion of the dye has been removed, it seems justifiable to assume that the sodium bitartrate has reduced some of the dye, and it is for this reason that the observed low results have been obtained on Amaranth, Ponceau 3R, and Sunset Yellow FCF, as well as on certain other dyes.

Curve 3, Figure 1, shows the results when Amaranth is titrated in the presence of concentrated hydrochloric acid as given in Department Bulletin 1390 (1). The jump in voltage

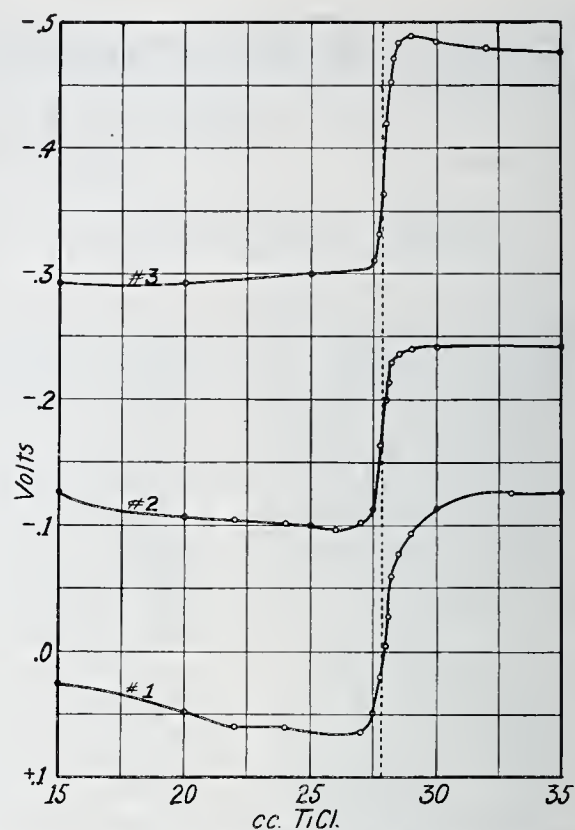


FIGURE 2. CURVES FOR ORANGE I USING THREE DIFFERENT BUFFERS. Curve 1, 0.1 gram + 5 grams of sodium bitartrate; curve 2, 0.1 gram + 5 grams of sodium citrate; curve 3, 0.1 gram + 5 grams of sodium bicarbonate

is not so sharp as when sodium citrate is used as a buffer, and slightly lower results are also obtained which are probably due to the fading of the Amaranth in the strongly acid solution. The electrometric-titration curves clearly demonstrate the superiority of sodium citrate over hydrochloric acid in this titration.

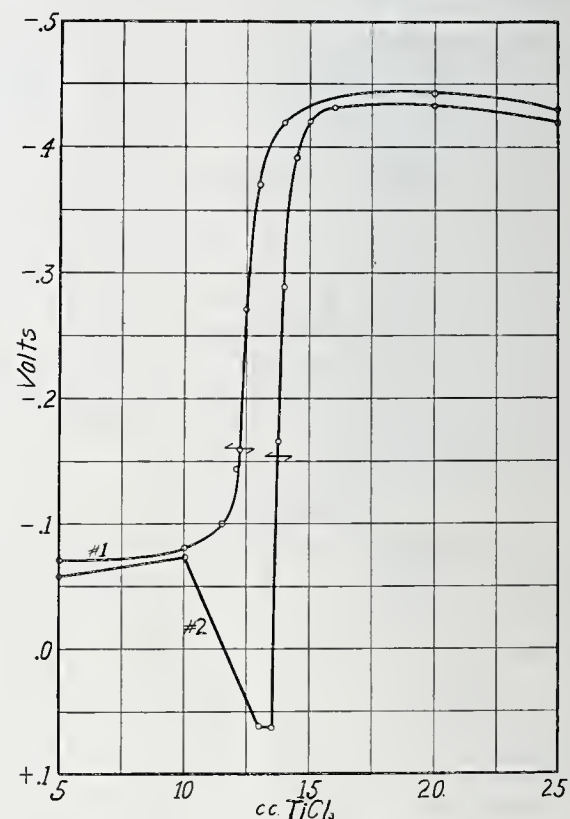


FIGURE 3. CURVES FOR LIGHT GREEN SF YELLOWISH AND GUINEA GREEN B. Curve 1, 0.2 gram of Light Green SF Yellowish + 5 grams of sodium bitartrate; curve 2, 0.2 gram of Guinea Green B + 5 grams of sodium bitartrate

Figure 2 shows typical curves obtained by titrating Orange I with three different buffers. The end point is indicated by the dotted line at 27.9 cc. and shows the close agreement of results when different buffers, which are suitable, are used. It is interesting to note that the more alkaline buffer produced a greater voltage in each case.

The curve obtained with sodium bicarbonate as a buffer again verifies the statement in a previous paper (4) that correct results may be obtained with this salt. It also demonstrates that the precipitate which forms in the titration flask when such an alkaline buffer is used does not effect the reduction.

Since the titration curves of the other monazo food dyes are very similar to those of Amaranth and Orange I, they are not presented here.

Curve 1, Figure 3, is a typical curve obtained by titrating Light Green SF Yellowish, a triphenylmethane dye. Curve 2, using Guinea Green B, illustrates an irregularity that was often encountered with the triphenylmethane dyes. By allowing a longer time for equilibrium to become established before recording the voltage, a curve more like curve 1 may be obtained. There is, however, no particular advantage in doing so, since the jump in potential apparently occurs at the same place in either case.

Figure 4 is presented to show typical results on two other dyes from other classifications and is self-explanatory.

When a mixture of two oxidizing agents is reduced, one will react completely before the other is attacked, provided there is a sufficient difference in the oxidizing power of the two. Tomicek (13) has investigated a number of such inorganic mixtures and has given 400 to 500 millivolts as approximately the difference in oxidation potential required before a successful electrometric titration can be made. With a suitable combination, the complete reduction of the first ion is indicated by a sharp jump in potential to another level at which the voltage remains until the second ion is reduced, when another sudden rise in potential occurs.

From a consideration of the possibility of titrating inorganic mixtures, as outlined above, the authors attempted to apply

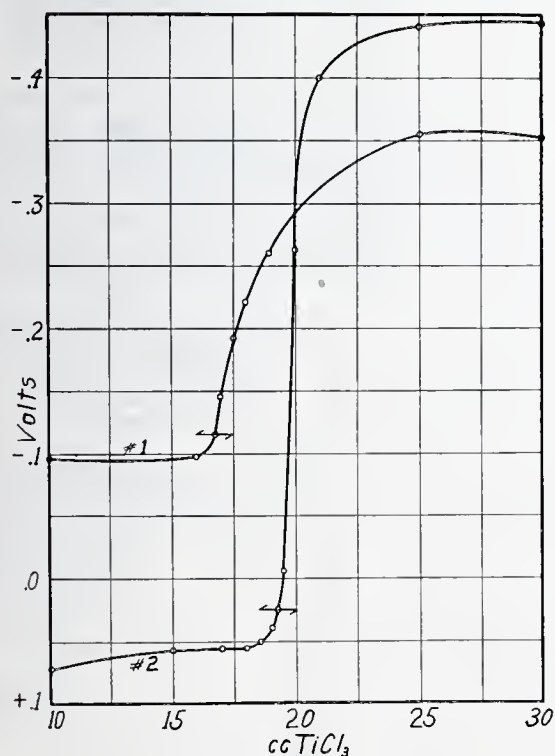


FIGURE 4. CURVES FOR NAPHTHOL YELLOW S AND TARTRAZINE. Curve 1, 0.02 gram of Naphthol Yellow S + 5 grams of sodium bitartrate; curve 2, 0.1 gram of Tartrazine + 5 grams of sodium bitartrate

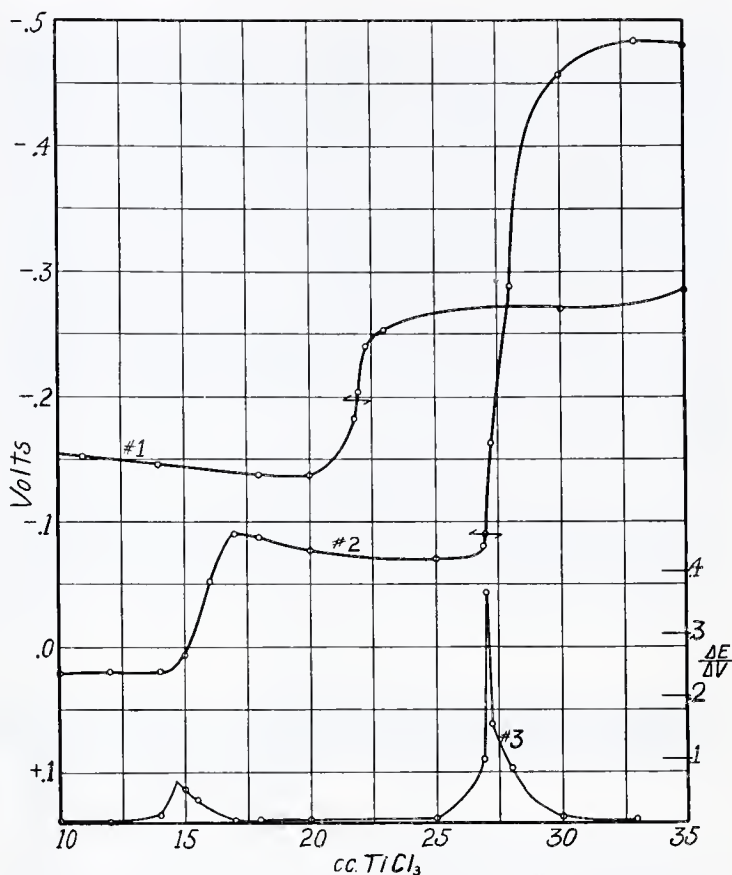


FIGURE 5. CURVES FOR CERTAIN MIXTURES. Curve 1, 0.05 gram of Amaranth + 0.05 gram of Orange I + 5 grams of sodium citrate; curve 2, 0.2 gram of Brilliant Blue + 0.05 gram of Orange I + 5 grams of sodium bitartrate; curve 3, same data as curve 2, using $\Delta E/\Delta V$ as one coordinate

the same principle to a mixture of food dyes. The first step in such a procedure would be to measure the oxidation potential of the individual dyes and from these values determine which mixtures it should be possible to separate, assuming that a difference of 400 to 500 millivolts in potential would be necessary, as in the case discussed above. It was found, however, that significant results could not be arrived at from the values observed. The reason probably is, as Conant and Biglow (3) have pointed out, that "the reduction of azo dyes and triphenylmethane dyes is of a different sort; here the reduction products are not rapidly reoxidized and no significant oxidation-reduction potentials can be measured by the usual method." It may be possible to establish the relative reactivity of these dyes by some modification of the methods which were employed, or by other means now under consideration in this laboratory, such as selecting a graded series of reducing agents and adjusting temperature, hydrogen ion, and concentration factors to a point where selective reduction would take place. This would not give the true oxidation potential of the dye, however, and hence it was not attempted in this electrometric study. This failure to measure the correct oxidation potential of the individual dyes left us without a systematic method of predicting which dye mixtures it should be possible to estimate by an electrometric titration.

In order to give concrete evidence as to the actual state of affairs, a number of mixtures were tried. In most cases no significant break occurred in the curve until both dyes had been reduced. Curve 1, Figure 5, shows the results on a mixture of Orange I and Amaranth and is a typical example. No jump in voltage occurred until both dyes had been reduced (at 21.9 cc.). Although not giving the amount of each dye present, the method may be used to determine the total titanium trichloride required to reduce the dyes present.

Results on a mixture of Orange I and Brilliant Blue FCF, shown on Figure 5, curve 2, indicate that in the case of some

mixtures satisfactory results may be obtained. By calculation, the Orange I present (0.05 gram) should be completely reduced when 14.2 cc. of the 0.0401 *N* titanium trichloride solution had been added. Correspondingly, the calculated end point for the total dye content should be at 27.0 cc., which is exactly the case. Curve 3 is plotted from the same data used in making curve 2, the difference being that *V* (cc. of TiCl_3 used) is plotted against the increment of the potential (ΔE) divided by the increment in volume of the reagent (ΔV). This method of plotting has been explained by Hostetter and Roberts (6). It gives a more satisfactory indication of the end point on a curve that does not have a sharp break and is applicable to all electrometric-titration curves.

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- (4) Evenson, O. L., and McCutchen, D. T., *IND. ENG. CHEM.*, 20, 860 (1928).
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- (11) Kolthoff, I. M., and Robinson, C., *Rec. trav. chim.*, 45, 169 (1926).
- (12) Kolthoff, I. M., and Tomicek, O., *Ibid.*, 43, 775 (1924).
- (13) Tomicek, O., *Ibid.*, 43, 808 (1924).

RECEIVED July 13, 1931. Ninth contribution from the Color Certification Laboratory, Food and Drug Administration, U. S. Department of Agriculture.

Recommended Specifications for Analytical Reagent Chemicals

Barium Acetate, Borax (Sodium Borate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), Cadmium Sulfate, Ferric Chloride, Ferric Nitrate, Litmus Paper, Potassium Bisulfate Fused

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THE specifications given below are intended to serve for reagents to be used in careful analytical work. The limits and tests are based on published work, on the experience of members of the committee in the examination of reagent chemicals on the market, and on studies of the tests made by members of the committee as the various items were considered. Suggestions for the improvement of the specifications will be welcomed by the committee.

In all the directions the acids and ammonium hydroxide referred to are of full strength unless dilution is specified; dilution indicated as (1 + 3) means 1 volume of the reagent or strong solution with 3 volumes of water; "water" means distilled water of a grade suitable for the test described; reagents used in making the tests are supposed to be of the grade recommended below or in previous publications (1-8) from the committee. Directions for the preparation of the ammonium molybdate solution are given under the test for phosphate in ammonium nitrate (3). A time of 5 minutes is to be allowed for the appearance of precipitates and before observation of color reactions, unless some other time is specified.

Blank tests must be made on water and all reagents used in the tests unless the directions provide for elimination of errors due to impurities. Solutions of samples must be filtered for tests in which insoluble matter would interfere.

BARIUM ACETATE

REQUIREMENTS

Insoluble Matter—Not more than 0.010 per cent.

Chloride (Cl)—Not more than 0.003 per cent.

Nitrate (NO_3)—To pass test (limit about 0.01 per cent).

Alkali Salts (as sulfates)—Not more than 0.10 per cent.

Calcium and Strontium Salts—Not more than 0.15 per cent.

Heavy Metals—To pass test (limit about 0.0005 per cent lead).
Iron (Fe)—Not more than 0.001 per cent.

TESTS

Insoluble Matter—Dissolve 10 grams in about 100 cc. of hot water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash thoroughly, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0010 gram.

Chloride—Dissolve 1 gram in 20 cc. of water and add 2 drops of nitric acid and 1 cc. of 0.1 *N* silver nitrate. The turbidity should not be greater than is produced by 0.03 mg. of chloride ion in an equal volume of solution containing the quantities of nitric acid and silver nitrate used in the test.

Nitrate—Dissolve 3 grams in 15 cc. of water, add 1 drop of indigo solution (1 in 1000), and add with constant stirring 15 cc. of sulfuric acid. The blue color should not be destroyed in 5 minutes.

Alkali Salts—Dissolve 5 grams in about 150 cc. of water, add 1 cc. of hydrochloric acid, and heat to boiling. Add 25 cc. of 2 *N* sulfuric acid, cool, make up to 250 cc., and allow to stand overnight. Decant through a filter, evaporate 100 cc. of the filtrate to dryness, ignite, and weigh the residue. The weight should not exceed 0.0020 gram.

Calcium and Strontium Salts—Dissolve 2 grams in 10 cc. of hot water, add 10 cc. of hydrochloric acid, and evaporate to dryness on the steam bath. Dissolve the residue in 10 cc. of hot water, add 10 cc. of hydrochloric acid, evaporate to dryness again, and dry in the oven at 105° C. Powder the residue and add 20 cc. of absolute alcohol. Allow to stand for 30 minutes with occasional shaking. Filter, evaporate the filtrate, ignite gently, and weigh. The weight of the residue should not exceed 0.0030 gram.

Heavy Metals—Dissolve 2 grams in 40 cc. of water, add 1 cc. of *N* hydrochloric acid, and pass hydrogen sulfide gas through the solution. No brown color should be produced. Observation of the color should be made within 2 minutes.

Iron—Add ammonium hydroxide to the solution tested for heavy metals until it is alkaline to litmus. Any green color should be no greater than is produced by 0.02 mg. of iron in an alkaline sulfide solution.

BORAX (SODIUM BORATE, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)

REQUIREMENTS

Insoluble Matter—Not more than 0.005 per cent.
Chloride (Cl)—Not more than 0.001 per cent.
Phosphate (PO_4)—Not more than 0.001 per cent.
Sulfate (SO_4)—Not more than 0.005 per cent.
Calcium (Ca)—To pass test (limit about 0.005 per cent).
Heavy Metals—To pass test (limit about 0.001 per cent as lead).
Iron (Fe)—Not more than 0.001 per cent.

TESTS

Insoluble Matter—Dissolve 10 grams in 150 cc. of water and heat on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash thoroughly, dry at 105° to 110°C. , and weigh. The weight of the residue should not exceed 0.0005 gram.

Chloride—Dissolve 1 gram in 15 cc. of warm water. Add 1 cc. of nitric acid and 1 cc. of approximately 0.1 *N* silver nitrate. Any turbidity produced at the end of 15 minutes should not be greater than is produced by 0.01 mg. of chloride ion in an equal volume of solution with the quantities of reagents used in the test.

Phosphate—Dissolve 5 grams in 75 cc. of water and add 10 cc. of nitric acid and 8 cc. of ammonium hydroxide. Warm to 60°C. , add 50 cc. of ammonium molybdate solution, and shake for 5 minutes. Any precipitate should not be greater than is produced in a solution of equal volume with the same quantities of reagents and 0.05 mg. of PO_4 .

Sulfate—Dissolve 8 grams in 120 cc. of warm water and 6 cc. of hydrochloric acid. Filter and wash with 30 cc. of water. Heat to boiling, add 5 cc. of 10 per cent barium chloride solution, and allow to stand overnight. Heat to dissolve any boric acid that may be crystallized. Filter, wash thoroughly, ignite, and weigh. The weight of the ignited precipitate should not be more than 0.0010 gram greater than the weight of the ignited precipitate from a blank made with the quantities of the reagents used in the test, including filtration and ignition of the paper.

Calcium—Dissolve 2 grams in 25 cc. of water and add 1 cc. of acetic acid and 5 cc. of 4 per cent ammonium oxalate solution. No turbidity should appear in 10 minutes.

Heavy Metals—Dissolve 2 grams in 25 cc. of hot water, add 0.5 cc. of hydrochloric acid, heat to about 80°C. , and add 5 cc. of hydrogen sulfide water. No darkening of the solution should be observed.

Iron—To the solution tested for heavy metals add ammonium hydroxide until it is alkaline to litmus. Any greenish color should not be greater than is produced by 0.02 mg. of iron in an alkaline sulfide solution.

CADMIUM SULFATE

REQUIREMENTS

Insoluble Matter—Not more than 0.005 per cent.
Chloride (Cl)—Not more than 0.001 per cent.
Nitrate (NO_3)—To pass test (limit about 0.005 per cent).
Arsenic (As)—Not more than 0.0002 per cent.
Copper (Cu)—To pass test (limit about 0.002 per cent).
Iron (Fe)—To pass test (limit about 0.001 per cent).
Lead (Pb)—To pass test (limit about 0.005 per cent).
Substances Not Precipitated by Ammonium Sulfide—Not more than 0.15 per cent.
Zinc (Zn)—To pass test (limit about 0.05 per cent).

TESTS

Insoluble Matter—Dissolve 10 grams in 150 cc. of water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash thoroughly, dry at 105° to 110°C. , and weigh. The weight of the residue should not exceed 0.0005 gram.

Chloride—Dissolve 1 gram in 10 cc. of water and add 1 cc. of nitric acid and 1 cc. of approximately 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.01 mg. of chloride ion with the same quantities of reagents.

Nitrate—To a solution of 1 gram in 10 cc. of warm water add about 10 mg. of sodium chloride, 2 drops of freshly prepared indigo solution (1 in 1000), and 10 cc. of sulfuric acid. The blue color should not be discharged in 5 minutes.

Arsenic—Test 5 grams by the Gutzeit method as described in the U. S. Pharmacopeia.

Copper and Iron—Dissolve 1 gram in 10 cc. of water, add 2 drops of nitric acid, bring to a boil, and allow to cool. Add 2 drops of a freshly prepared 10 per cent solution of potassium

ferrocyanide. No red or blue color should be produced after standing 15 minutes.

Lead—Dissolve 1 gram in 25 cc. of water, add 5 drops of glacial acetic acid, and filter if necessary. Add 1 cc. of 1 per cent potassium chromate solution. Any turbidity or precipitate should not be greater than is produced by 0.05 mg. of lead under the same conditions.

Substances Not Precipitated by Ammonium Sulfide—Dissolve 2 grams in 150 cc. of water, add ammonium hydroxide to dissolve the precipitate first formed, and pass hydrogen sulfide gas through the solution to precipitate all the cadmium. Filter off 75 cc. of the clear liquid, add 5 drops of sulfuric acid, evaporate to dryness, and ignite gently. The weight of the ignited residue should not be more than 0.0015 gram.

Zinc—Dissolve 0.2 gram in 100 cc. of water and add 3.5 cc. of sulfuric acid. Heat to boiling and pass a rapid stream of hydrogen sulfide for 15 minutes, allowing the solution to cool during the passage of the gas. Filter at once, evaporate the filtrate, and expel practically all of the sulfuric acid. Take up the residue with 5 cc. of water and add ammonium hydroxide until the solution is just alkaline to litmus paper. Then make it just acid to the litmus paper with 0.1 *N* sulfuric acid. Dilute to 100 cc. and pass a rapid stream of hydrogen sulfide for 5 minutes. No white precipitate or turbidity should be produced.

FERRIC CHLORIDE

REQUIREMENTS

Insoluble Matter—Not more than 0.010 per cent.
Nitrate (NO_3)—To pass test (limit about 0.01 per cent).
Phosphorus Compounds—Not more than 0.030 per cent as PO_4 .
Sulfate (SO_4)—Not more than 0.005 per cent.
Arsenic (As)—To pass test (limit about 0.002 per cent).
Copper (Cu)—To pass test (limit about 0.003 per cent).
Ferrous Iron (Fe)—To pass test (limit about 0.002 per cent).
Substances Not Precipitated by Ammonium Hydroxide—Not more than 0.10 per cent.
Zinc (Zn)—To pass test (limit about 0.003 per cent).

TESTS

Insoluble Matter—Dissolve 10 grams in 50 cc. of water and 1 cc. of hydrochloric acid and heat on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash with warm water containing about 0.5 per cent of hydrochloric acid until the washings are free of iron, dry at 105° to 110°C. , and weigh. The weight of the insoluble residue should not exceed 0.0010 gram.

Phosphorus Compounds—To 5 grams add 20 cc. of water and 20 cc. of nitric acid and evaporate on the steam bath to a sirup. Add 50 cc. of water, 15 cc. of nitric acid, and 13 cc. of ammonium hydroxide. Add 50 cc. of ammonium molybdate solution, shake for 5 minutes at 40° to 50°C. , and allow to stand for 1 hour. Any precipitate formed should not be greater than is formed under the same conditions by 1.5 mg. of PO_4 .

Nitrate, Sulfate, and Substances Not Precipitated by Ammonium Hydroxide—

Solution A: Dissolve 10 grams in 100 cc. of water. Heat to boiling and pour into a mixture of 140 cc. of water and 50 cc. of ammonium hydroxide. Filter through a folded filter while still hot and wash with hot water until the filtrate (solution A) measures 300 cc.

Nitrate: Mix 15 cc. of solution A with 15 cc. of sulfuric acid and add 2 drops of indigo solution (1 in 1000). The blue color should not disappear in 5 minutes.

Sulfate: Evaporate 120 cc. of solution A to 50 cc. and add 0.5 cc. of dilute hydrochloric acid (1 + 2). Prepare a standard of equal volume containing 20 cc. of ammonium hydroxide, which has been boiled to expel the ammonia, 0.20 mg. of SO_4 , and 0.5 cc. of dilute hydrochloric acid (1 + 2). Add 3 cc. of 10 per cent barium chloride to each solution. After 10 minutes the turbidity produced by the sample should not be greater than that produced by the standard.

Substances Not Precipitated by Ammonium Hydroxide: Evaporate 30 cc. of solution A to dryness. Add 10 drops of sulfuric acid and ignite cautiously. The weight of the residue should not exceed 0.0010 gram.

Arsenic—Dissolve 1 gram in 0.5 cc. of hydrochloric acid and add 5 cc. of freshly prepared stannous chloride solution. Warm to 70° to 80°C. for 5 minutes and allow to stand for an additional 25 minutes. At the end of this time the solution should not be noticeably darker than a mixture prepared with the same quantities of ferric chloride and stannous chloride solution immediately before observing the test.

The stannous chloride solution used in this test is made by saturating hydrochloric acid with stannous chloride.

Copper and Zinc—Neutralize 90 cc. of solution A with acetic acid and add an excess of 1 cc. of glacial acetic acid and 2 cc. of freshly prepared 10 per cent solution of potassium ferrocyanide. No turbidity or pink color should appear in 30 minutes.

Ferrous Iron—Dissolve 0.5 gram in a mixture of 20 cc. of water and 1 cc. of hydrochloric acid and add 1 drop of a freshly prepared 5 per cent solution of potassium ferricyanide. No blue color should be produced in 1 minute.

FERRIC NITRATE

REQUIREMENTS

Insoluble Matter—Not more than 0.010 per cent.

Chloride (Cl)—Not more than 0.001 per cent.

Sulfate (SO₄)—Not more than 0.010 per cent.

Substances Not Precipitated by Ammonium Hydroxide—Not more than 0.10 per cent.

TESTS

Insoluble Matter—Dissolve 10 grams in a mixture of 100 cc. of water and 1 cc. of nitric acid and heat on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash thoroughly, and dry at 105° to 110° C. The weight of the residue should not exceed 0.0010 gram.

Chloride—Dissolve 2 grams in 15 cc. of water and add 1 cc. of nitric acid. To 15 cc. of water add 1 cc. of nitric acid and hydrochloric acid equivalent to 0.02 mg. of chloride. Add to each solution 1 cc. of 0.1 N silver nitrate. The sample should not be more turbid than the standard.

Sulfate and Substances Not Precipitated by Ammonium Hydroxide—

Solution A: Dissolve 5 grams in 70 cc. of water and pour it into a mixture of 15 cc. of ammonium hydroxide and 80 cc. of water. Filter through a folded filter and wash with hot water until the filtrate measures 250 cc.

Sulfate: Evaporate 100 cc. of solution A to 50 cc. and add 0.5 cc. of dilute hydrochloric acid (1 + 2). Prepare a standard of equal volume containing 6 cc. of ammonium hydroxide, which has been boiled to expel the ammonia, 0.20 mg. of SO₄, and 0.5 cc. of dilute hydrochloric acid (1 + 2). Add 3 cc. of 10 per cent barium chloride to each solution. After 10 minutes the turbidity produced by the sample should not be greater than that produced by the standard.

Substances Not Precipitated by Ammonium Hydroxide: Evaporate 50 cc. of solution A to dryness, add 10 drops of sulfuric acid, and ignite carefully. The weight of the residue should not exceed 0.0010 gram.

LITMUS PAPER

REQUIREMENTS

Ash—Not more than 0.4 mg. per strip (about 3 sq. cm.).

Rosin Acids, etc. (for blue paper only)—To pass test.

Sensitiveness—To pass test.

TESTS

Ash—Ignite carefully 10 strips. The ash should not be more than 0.0040 gram.

Rosin Acids, etc.—Immerse a strip of blue paper in a solution of 0.10 gram of silver nitrate in 50 cc. of water. The color should not change in 30 seconds.

Sensitiveness—Drop a piece of the paper into 100 cc. of test solution in a beaker and stir continuously. A blue paper should change color in 45 seconds in 0.0005 N acid. A red paper should change color in 30 seconds in 0.0005 N alkali.

POTASSIUM BISULFATE FUSED

REQUIREMENTS

Acidity—Not less than 34.0 per cent, nor more than 36.0 per cent as H₂SO₄.

Insoluble Matter and Ammonium Hydroxide Precipitate—Not more than 0.010 per cent.

Chloride (Cl)—Not more than 0.002 per cent.

Phosphate (PO₄)—Not more than 0.001 per cent.

Arsenic (As)—Not more than 0.0005 per cent.

Calcium and Magnesium Precipitate—Not more than 0.005 per cent.

Heavy Metals—To pass test (limit about 0.0005 per cent lead).

Iron (Fe)—Not more than 0.002 per cent.

TESTS

Acidity—Dissolve 4 grams in 50 cc. of water and titrate with normal alkali.

Insoluble Matter and Ammonium Hydroxide Precipitate—Dissolve 10 grams in 100 cc. of water, add ammonium hydroxide until the solution is alkaline to methyl red, boil for 1 minute, and digest on the steam bath for 1 hour. Filter through asbestos

in a Gooch crucible, wash thoroughly, and dry 1 hour at 105° to 110° C. The weight of the precipitate should not be more than 0.0010 gram.

Chloride—Dissolve 1 gram in 15 cc. of water and add 2 cc. of nitric acid and 1 cc. of 0.1 N silver nitrate. Any turbidity should not be greater than is produced by 0.02 mg. of chloride ion in an equal volume of solution containing the quantities of reagents used in the test.

Phosphate—Dissolve 5 grams in 50 cc. of water, add 10 cc. of nitric acid, and nearly neutralize with ammonium hydroxide. Add 50 cc. of ammonium molybdate solution, shake (at about 40° C.) for 5 minutes, and allow to stand one-half hour. Any precipitate formed should not be greater than is produced when a quantity of an alkali phosphate containing 0.05 mg. of phosphate (PO₄) is treated according to the above procedure.

Arsenic—Determine on a 0.5-gram sample by the modified Gutzeit method.

Calcium and Magnesium Precipitate—To the filtrate from the test for insoluble matter (without the washings) add 5 cc. of 4 per cent ammonium oxalate solution, 3 cc. of 10 per cent ammonium phosphate solution, and 10 cc. of ammonium hydroxide. If any precipitate forms on standing overnight, filter, wash thoroughly with water containing 2.5 per cent of NH₃, ignite, and weigh. The weight should not be more than 0.0005 gram.

Heavy Metals—Dissolve 2 grams in 25 cc. of water, add 2 cc. of hydrochloric acid, and boil gently for 10 minutes. Cool, neutralize to litmus with ammonium hydroxide, add 1 cc. of 0.1 N hydrochloric acid, dilute to 25 cc., and pass hydrogen sulfide through the solution. No brown color should appear.

Iron—Add ammonium hydroxide to the solution obtained in the test for heavy metals until it is slightly alkaline. Any green color produced should not be greater than is produced by 0.04 mg. of iron in an equal volume of alkaline sulfide solution.

CORRECTIONS FOR PUBLISHED SPECIFICATIONS

Replace the requirements and tests previously printed by the following:

MAGNESIUM OXIDE (8)

TESTS

Chloride—Add 0.5 gram of the sample to a mixture of 10 cc. of water and 3 cc. of nitric acid.

METHANOL (5)

REQUIREMENT

Acetone, Aldehydes—To pass test (limit about 0.003 per cent acetone).

TEST

Acetone, Aldehydes—Make comparison with 0.030 mg. of acetone.

POTASSIUM IODATE (3)

TEST

Chloride and Bromide—Second sentence should read, "Treat the residue with 10 cc. of hot water and 1 cc. of dilute nitric acid (1 + 4), filter, and wash with 10 cc. of hot water." Make comparison with 0.10 mg. of chloride.

POTASSIUM BROMIDE (3)

TEST

Iron—Make comparison with 0.01 mg. of iron.

SODIUM BISULFATE FUSED (5)

TEST

Arsenic—Use a sample of 0.50 gram.

SPECIFICATIONS PREVIOUSLY PUBLISHED

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Measurement of Average Particle Size of Fine Pigments

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THE reinforcing properties of pigments used in rubber compounding and the milling characteristics of these pigments are so intimately connected with their degree of fineness that considerable interest is attached to securing measurements of their average particle size. Much work has been done on the measurement of the particle size of microscopic and ultra-microscopic material, and a number of methods have been devised which, when properly used, yield satisfactory results. Svedberg (24) gives an excellent discussion of these methods. Similarly, Green (11) gives a very complete discussion of the theory of average particle size and the significance of average diameters, and Wells (27) a résumé of the field of turbidity measurements.

The particle size of rubber pigments ranges from the definitely microscopic well into the colloidal region. Two of the most important are carbon black and zinc oxide, and it is these pigments which have been investigated most thoroughly, although a few others of interest have been studied.

Considerable work has been done on the determination of the particle size of carbon black, but the literature contains varying figures. The value given by Spear (21), $0.1\text{--}0.2\mu$ up to about 0.6μ , has been widely quoted. Green (9) gives the size of gas black as about 0.15μ . Peterfi, for A. Wegelin (26), determined by the Zsigmondy count method the average particle size of three German carbon blacks as 0.124 , 0.106 , and 0.083μ . More recently (for F. Hartner, 13) he gives 0.050μ for the average diameter of gas black. J. J. Barnard, in a communication to Wiegand (28), reports by ultra-filtration and counting in ultra-violet

A method of obtaining excellently dispersed suspensions of rubber pigments of accurate concentration is described in which the pigment is milled into rubber and the stock then dissolved in a solvent.

The average particle sizes of carbon blacks measured by the Zsigmondy count method were found to range from 0.061μ for rubber gas black to 2.22μ for the coarsest one measured. The zinc oxide pigments had average particle sizes from 0.076μ to 0.57μ . Measurements on several other pigments of interest are included. Because of the high visibility in the ultra-microscope, this method gives smaller values for average particle size than the photomicrographic methods.

The results have been used to calibrate a microturbidimeter of the extinction type for use in measuring average particle size.

Curves are included showing how the turbidities of suspensions of zinc oxide and carbon black vary with the average particle size, concentration, and wave length of light used.

light an estimated average particle size of gas black as $0.05\text{--}0.06\mu$. Grenquist (12) estimated gas black as ranging from 0.015 to 0.200μ .

Parkinson (17) makes no estimate of the particle size of gas black, but quotes the particle size of lampblack as about $0.3\text{--}0.6\mu$, which agrees well with Green's estimate, $0.3\text{--}0.4\mu$. Moore (15) gives for the particle size of Thermatomic black, 1.0μ , and for P-33, 0.23μ .

Most of the results which have been published on the average particle size of zinc oxide pigments have been obtained by Green's (11) photomicrographic method or modifications thereof. In the papers of Green (10, 11), Haslam and Hall (14), and Stutz and Pfund (23) can be found a large number of measurements for every type of zinc oxide. The values quoted in Table III, supplied by the New Jersey Zinc Co., were obtained by the

method of Stutz and Pfund (23).

It is the purpose of this paper to set forth an accurate and efficient method for measuring particle size. Since the authors are directly concerned with the particle size of rubber pigments as dispersed in rubber, and not as dispersed in an aqueous medium or rubbed out on a slide, the turbidity of xylene-rubber-pigment cements prepared by milling the pigment into the rubber and swelling in xylene has been used as the basis of this method. The turbidimeter used in this work was the microturbidimeter used previously by Gehman and Ward (7).

Since the turbidity of suspensions is affected by a number of variables not readily calculable, a turbidimeter to be used for particle-size measurements must be calibrated with pigments whose particle size has been determined by an inde-

pendent method. For calibration of the turbidimeter the count method with the cardioid ultra-microscope of Siedentopf (18), manufactured by Zeiss, has been used.

Average particle sizes as determined by the count method together with turbidimetric measurements have been obtained on a series of carbon blacks, a series of zinc oxides, and a few other pigments of interest in the rubber industry. The carbon blacks used varied in particle size from 0.025 to 2.22 μ , and the zinc oxides from 0.076 to 0.566 μ .

THEORY OF MICROTURBIDIMETER

The microturbidimeter is an extinction type of turbidimeter. When the light from the filament enters a suspension of a white pigment, it undergoes a loss of intensity because of light scattering by the disperse phase. The process of

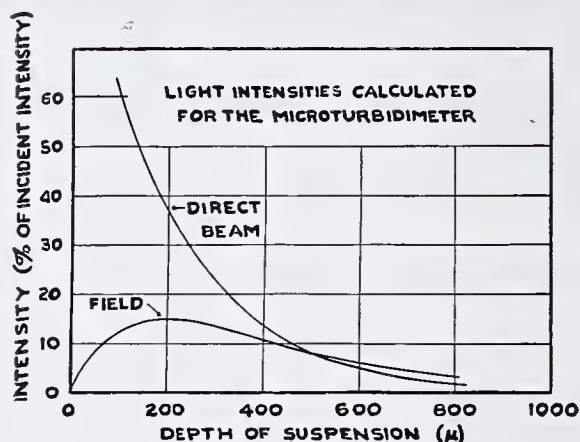


FIGURE 1

extinction consists in having the diffuse field due to the scattered light of the same intensity as the direct beam. The way in which the scattered intensity and direct intensity vary to produce this result is explained as follows:

Let I_0 = intensity of incident beam before any scattering
 I_x = intensity of incident beam after penetrating a depth x
 I_s = intensity of forward scattered light at x

Also let dI_s be the light scattered in the forward direction from an element of depth dx which we think of as having unit cross section. The intensity dI_s will be diminished exponentially as it proceeds in the direction of x , according to Lambert-Beer's well-known law (25).

The intensity of the direct beam at x will be, in accordance with the same law

$$I_x = I_0 e^{-kx} \quad (1)$$

k is a constant for any one suspension, concentration, and wave length. The increment of scattered light, dI_s , will be proportional to $I_0 e^{-kx}$ and to dx . Hence

$$dI_s = A I_0 e^{-kx} dx \quad (2)$$

A is a constant.

By the time dI_s penetrates to a depth d , its intensity will be $dI_s e^{-k(d-x)}$, assuming monochromatic light. This will be its contribution to the intensity of the scattered light at d .

The total intensity of the scattered light will be the integral of all the contributions from the small elements between $x = 0$ and $x = d$, hence

$$I_s = \int_0^d e^{-k(d-x)} dI_s$$

From Equation 2

$$\begin{aligned} I_s &= \int_0^d e^{-k(d-x)} A I_0 e^{-kx} dx \\ I_s &= \int_0^d A I_0 e^{-kd} e^{kx} e^{-kx} dx \\ I_s &= A I_0 d e^{-kd} \end{aligned} \quad (3)$$

To a first approximation this is the intensity of the forward scattered light at depth d .

When the intensity of the direct beam equals the intensity of the scattered light—i. e., at the extinction depth d_s —we have

$$\begin{aligned} I_x &= I_s \\ I_0 e^{-kd_s} &= A I_0 d_s e^{-kd_s} \\ A &= \frac{1}{d_s} \end{aligned}$$

So A is the reciprocal of the extinction depth.

Introducing this value of A in Equation 3, we get the intensity of the forward scattered light at depth d to be

$$I_s = I_0 \frac{d}{d_s} e^{-kd} \quad (4)$$

I_s has a maximum for a value of d which can be obtained by differentiating Equation 4 and equating to zero. The result which comes out of this procedure is that the scattered light has its maximum intensity for a value of d equal to $1/k$.

Figure 1 is a plot of Equations 1 and 4 for arbitrarily assumed values of k and d_s , and helps to visualize how the intensity of the scattered light and of the direct beam vary so as to achieve equality at one point—i. e., where the curves intersect. k was taken equal to 0.005 and d_s to 500 μ in order to plot the curves.

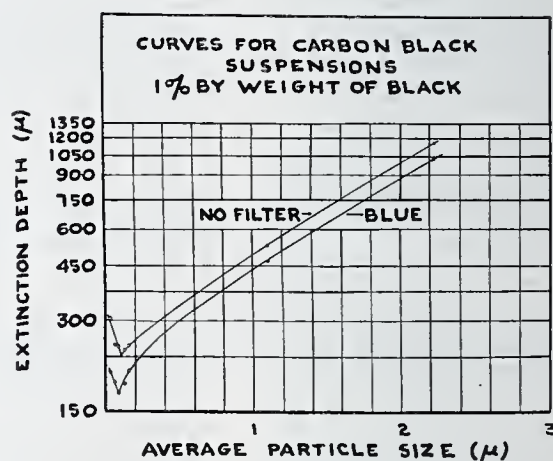


FIGURE 2

Equations 4 and 1 express the fact that the extinction depth is independent of the filament intensity. This is the case for white pigments and for latex. Since it is not strictly true for carbon black suspensions (see Figure 5), the equations would have to be modified for the cases where light absorption is important.

CALCULATION OF PARTICLE SIZE FROM ADHESION-TENSION MEASUREMENTS

Superspectra gas black is so fine that the ultra-microscope was not suitable for its measurement, as the results obtained indicated that it was but slightly smaller than Micronex, whereas other properties indicated that it was much smaller. An estimate of the average particle size for a series of blacks, one of which is similar to Superspectra, can be made from data which have been published by Bartell and Smith (3) on the pore radii of carbon black diaphragms used in adhesion-tension measurements. The method used in making this estimate is as follows:

Let n = number of particles per unit volume
 R = radius of pores
 x = number of pores per unit surface
 r = radius of particle
 d = diameter of particle
 v = volume in unit volume unoccupied by particles

The work of Smith, Foote, and Busang (20) on the packing of spherical lead shot under various conditions showed that a mean exists between cubic and hexagonal packing depending upon the method of packing, high-pressure packing approaching the hexagonal. They have worked out v for cubic packing as 0.4764, and for hexagonal packing 0.2595. For both types of packing, since there will be $\sqrt[3]{n}$ particles along an edge of a unit cube, $x = n^{2/3}$.

Using these facts, we have for the two types of packing the following equations:

CUBIC PACKING	HEXAGONAL PACKING
$n = \frac{1}{8r^3}$	$n = \frac{\sqrt{2}}{8r^3}$
$x = \frac{1}{4r^2}$	$x = \frac{\sqrt[3]{2}}{4r^2}$
$v = \pi R^2 x$	$v = \pi R^2 x$
$v = \frac{1}{4r^2} \pi R^2$	$v = \frac{\sqrt{2}}{4r^2} \pi R^2$
$0.4764 = \frac{\pi R^2}{4r^2}$	$0.2595 = \frac{\sqrt{2}}{4r^2} \pi R^2$
$d = 2.568R$	$d = 3.907R$

Table I gives the values of pore radii reported in a paper by Bartell and Smith (3) on the adhesion tension of a series of blacks, together with the values computed from them of the particle diameters on the assumption of hexagonal packing and on the assumption of cubic packing. It is interesting to note that the value for rubber gas black is of the same order as that secured by the ultra-microscopic count method. On the assumption that Superspectra was about the same as the specimen designated "color gas black," the value of 0.025μ has been introduced into Table II as being the best estimate available for the particle size of this black.

TABLE I. PARTICLE SIZE FROM PORE RADII MEASUREMENTS

SAMPLE	SOURCE	PORE RADIUS μ	LIMITS OF PARTICLE SIZE	
			Hexagonal packing μ	Cubic packing μ
A	Lampblack	0.0793	0.316	0.204
B	Thermal decomposition	0.0780	0.305	0.200
C	Thermal decomposition	0.0226	0.089	0.058
D	Rubber gas black	0.0173	0.068	0.045
E	Ink gas black	0.0190	0.075	0.049
F	Ink gas black	0.0183	0.072	0.047
G	Color gas black	0.0076	0.030	0.020

PREPARATION OF SUSPENSIONS

Aqueous suspensions of carbon black containing saponin and gum arabic as protective colloids milled in a small ball mill proved unreliable, since the turbidimeter readings depended on the time of milling and the amount of protective colloid. On the other hand, it was found that carbon black dispersed in rubber, remilled several times, and then made into a xylene cement, was completely deflocculated, and that readings could be duplicated closely. This technique was therefore adopted for all the pigments studied in the preparation of the suspensions for the turbidimeter. The carbon blacks were selected to cover the entire range from the coarsest to the finest. The carbon black was incorporated on an 18-inch laboratory mill.

The rubber was broken down on a warm mill. The carbon black was added until the batch came exactly to the desired weight. It was then cooled, remilled, cooled, and milled with an equal weight of clean pale crepe sheet. This batch was remilled until the dispersion was shown to be complete by microscopic examination using the squeeze-out method (1). In the case of Superspectra it was found necessary to dilute the stock further in order to get a smooth cement free from aggregates.

Xylene cements were then made up of the entire series of stocks, 1 per cent carbon black, 4 per cent rubber by weight, or 0.482 per cent carbon black by volume. The weighing was done on an analytical balance. Cements of different concentrations were prepared similarly. The cements were allowed to stand with occasional shaking until the dispersion appeared to be complete by microscopic examination.

The dispersions of zinc oxide were prepared in essentially the same manner by milling equal weights of zinc oxide and pale crepe rubber until microscopic examination by the squeeze-out method showed the dispersions to be satisfactory. Cements were then prepared of the desired concentrations by dissolving weighed amounts of stock in weighed quantities of xylene. All of the cements were examined microscopically to be sure the dispersions were complete.

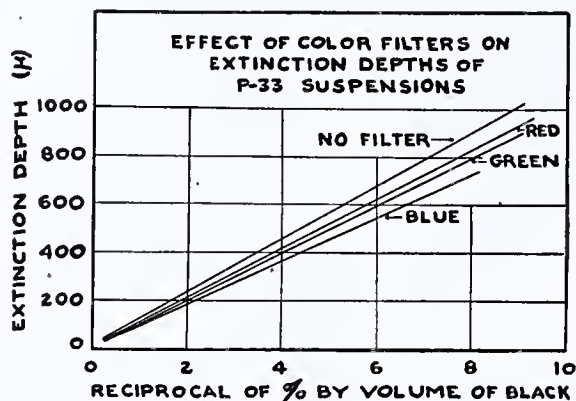


FIGURE 3

To secure very concentrated suspensions, evaporation of the more dilute cements was resorted to. A few cements in carbon disulfide and gasoline were prepared in the same manner as in xylene, the concentrations being calculated on a volume per cent basis to make them comparable with the xylene cements.

COUNTING PROCEDURE

With the invention of the slit ultra-microscope by Siedentopf and Zsigmondy (19), measurement of the particle size of colloids was first made possible. In the slit ultra-microscope the light enters the colloidal suspension at right angles to the axis of the microscope, the presence of the colloidal particle being indicated by a point of light on a dark background. Subsequent improvements such as the cardioid ultra-microscope of Siedentopf (18), the system used in the present investigation, have increased the usefulness of the instrument by increasing the resolving power of the system. The cardioid ultra-microscope differs from the slit ultra-microscope in that the illuminating pencil and diffracting pencil of rays which go to form the image are coaxial; the rays of greater aperture are employed to illuminate the object while those of smaller aperture are made to reach the eye, resulting in a brighter image.

The Zeiss cardioid ultra-microscope consists of a cardioid dark-ground condenser, a fused quartz counting chamber with holder, a 3-mm. glycerol immersion objective having a maximum N.A. of 1.0 with an iris aperture stop, and a 30X positive eyepiece all readily adapted to any microscope equipped with a substage rack. A clock-feed carbon arc with a water-cell heat filter was used for the illuminating system.

For estimation of the particle size a restricted volume of known dimensions is necessary. This was obtained by inserting in the ocular an Ehrlich stop giving a field 0.0163 mm. square. The depth of the cell was measured by focusing and was found to be 5.0μ .

In using the cardioid ultra-microscope, one of the prime

essentials is that the cell be absolutely clean. It was cleaned by boiling in cleaning solution, washing in hot distilled water, drying over a hot plate, and heating for a short time in a Bunsen flame. The system was aligned by an eccentric objective centering mount and the illumination centered by reflecting the image of the crater back into the arc. A drop of the suspension was placed in the cell which was clamped in the holder. The condenser was connected to the cell with a drop of water, the objective to the cell with a drop of glycerol, and the system adjusted until the images appeared as brightly illuminated, sharply defined spots against a dark background.

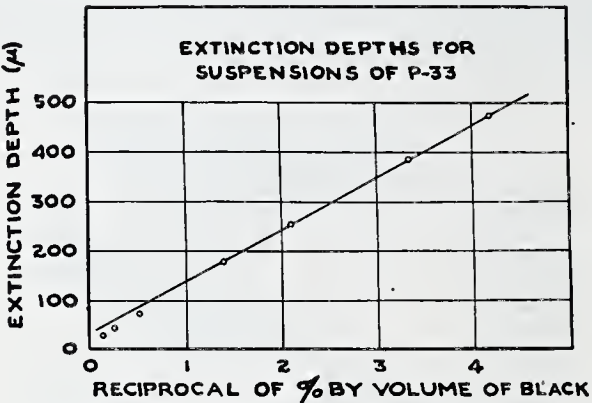


FIGURE 4

The suspensions for counting were prepared by dispersing one or two drops of the xylene cement in an appropriate weight of Nujol, the amounts being carefully weighed on an analytical balance. After standing a day or so with occasional shaking, complete dispersion was obtained. These cements are highly useful for counting, since Nujol itself is optically empty and the Brownian motion of the particle is almost completely stopped. Since rubber itself is not optically empty, a blank rubber cement was dispersed in Nujol at a somewhat higher concentration than that used for counting, the count averaging less than one particle per field, owing to the high dilution. The concentrations of the Nujol cements for counting were adjusted so as to yield as near 20 particles per field as possible. Usually twenty fields were counted and the averages obtained were duplicable.

SAMPLE CALCULATION WITH MICRONEX GAS BLACK

Wt. of xylene cement, 1% black by wt., gram.....	0.0229
Wt. of Nujol, grams.....	49.1335
Density of Nujol at 25° C.....	0.8848
Density of black.....	1.80
Av. of 20 fields, particles per field.....	25

$$D = \frac{1}{0.0001} \sqrt[3]{\frac{6CV}{\pi\rho n}}$$

Where D = average diameter in μ
 C = concentration of pigment, grams per cc.
 V = volume of field counted
 ρ = density of pigment
 n = average count

$$D = \frac{1}{0.0001} \sqrt[3]{\frac{6 \left(\frac{0.0229}{49.1335} \right) (0.01) (0.8848)}{(3.1416)(1.8)(25)}}$$

$$D = 0.061\mu$$

DISCUSSION OF MICROSCOPICAL METHODS

Results obtained by the count method would be expected to be smaller than those given by the photomicrographic method for the following reasons:

In the ultra-microscope, particles as small as 0.010 to 0.015 μ can be rendered visible since the perception of the particles depends rather on the following factors (24) than on the resolving power: (1) specific intensity of light source,

(2) aperture of illuminating system, (3) contrast in the field of view, and (4) light-emitting power of particles.

In photomicrographic methods, on the other hand, the numerical aperture of the objective limits the size of the smallest particles resolved to about 0.2 μ for visible light and 0.1 μ for ultra-violet light.

In the ultra-microscopic count method for the determination of particle size, the depth of the counting chamber is always a source of possible error. Since it is only a few microns in depth, it taxes to the limit most methods of micrometry. Several methods for measuring the cell depth have been tried, including the use of an adaptation of the optical lever of Bond (4). By this device a value of 2.0 $\mu \pm 0.2\mu$ was obtained for the difference in height between the center and edge of the cell chamber. But when the cell was assembled focusing on the upper and lower surfaces of the chamber with the microscope fine adjustment gave an average value of 5.0 μ , which is somewhat higher than the average value of all methods used and may be considered as a maximum. This value has been used for all calculations.

When the cell is filled with the Nujol counting cement, no correction for refractive index is necessary since the system is virtually homogeneous. A fortunate aspect of the situation is that in calculating the average diameter the depth of the cell enters into the formula as the cube root. It may be stated that the probable limit of accuracy of the method is ± 10 per cent, owing to errors in counting and measurements of the counting volume.

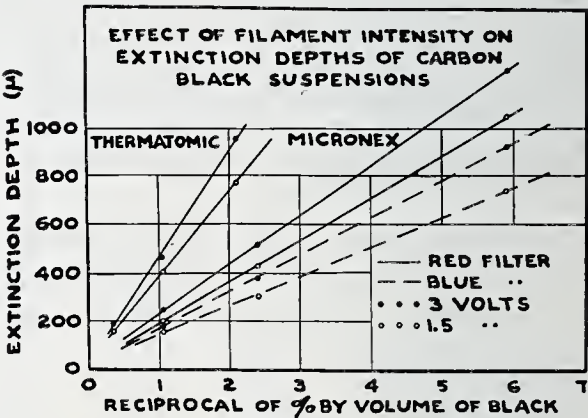


FIGURE 5

Although the photomicrographic method may be an excellent and useful one for coarse pigments, the authors believe that the finer pigments are actually much smaller than this method would indicate, for three reasons:

1. Particles of the finer pigments are near the limit of resolution for visible light, and the full theoretical resolving power of a system is rarely realized. A pigment whose average particle size is at the limit of resolution will have a large number of particles which are too small for resolution. Particles below the limit of resolution will appear enlarged (2).
2. It is impossible to get all the particles in the same focal plane, and since objectives of high N. A. have a very slight focal depth, enlarged images and circles of confusion will result.
3. No present method of preparing slides will yield as complete a dispersion as can be obtained by other means, such as milling the pigment into rubber.

For pigments for which direct illumination is suitable, the method of Dunn (6), in which the image is projected on a screen and thereby permits one to focus the particle being measured, seems preferable to the regular photomicrographic procedure.

RESULTS

In Tables II, III, and IV are given the average particle sizes, obtained by the count method, of the pigments used in calibrating the turbidimeter. Superspectra, listed in Table

II, is a special gas black known as a color black, and Micronex is a regular rubber gas black. P-33, Thermatomic, and Velvetex are all thermal-decomposition blacks supplied to the rubber trade, and are known as soft blacks.

TABLE II. PARTICLE SIZE OF CARBON BLACK PIGMENTS OBTAINED BY COUNT METHOD

PIGMENT	AV. PARTICLE SIZE μ
Superspectra ^a	0.025
Micronex	0.061
Special sample (rubber gas black)	0.092
Shewinnegan acetylene black	0.130
P-33	0.159
Thermatomic ^b	1.12
Velvetex ^b	2.22

^a Estimated.

^b Counted in blood count cell.

TABLE III. PARTICLE SIZE OF ZINC OXIDE PIGMENTS OBTAINED BY COUNT METHOD

PIGMENT	—AVERAGE PARTICLE SIZE— N. J. Zinc Co. values	Count method
	μ	μ
1	0.11	0.076
2	0.15	0.099
3	0.28	0.159
4	0.32	0.185
5	0.70	0.566

TABLE IV. PARTICLE SIZE OF MISCELLANEOUS RUBBER PIGMENTS OBTAINED BY COUNT METHOD

PIGMENT	PARTICLE SIZE μ
Red iron oxide	0.139
Titanium oxide	0.190
Blanc fixe	0.245
Special blanc fixe	0.160

All of the zinc oxides, together with the values for the particle size as obtained by the method of Stutz and Pfund (23), have been supplied by the New Jersey Zinc Co. The pigments appearing in Table IV are regular commercial grades.

DISCUSSION OF TURBIDIMETER MEASUREMENTS

The microturbidimeter used in this work has previously been described in detail (5, 7). It operates on the extinction principle. An incandescent filament is viewed through a film of the suspension contained between a convex lens and a flat glass plate. The turbidity of the suspension is measured by the depth of it required to produce extinction of the filament, or rather, by the reciprocal of this depth.

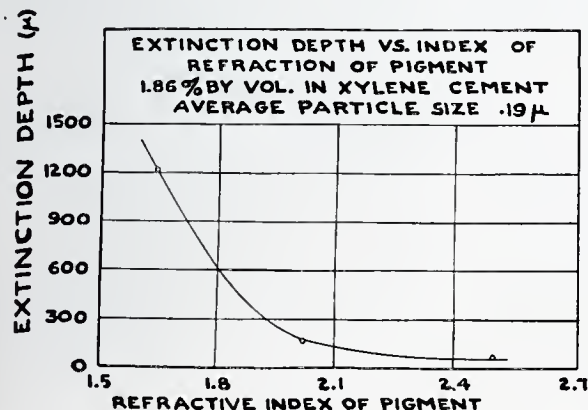


FIGURE 6

The radius of curvature of the lens used in the extinction cell of the turbidimeter was 8.636 cm. Red, green, and blue color filters were used. The red filter was a Wratten filter. The green was a Corning filter known as Sextant Green. For a blue filter, a combination of Corning light theater blue and dark heat-resisting blue was used. Unless the green and blue filters used with the microturbidimeter are very free from red transmission, as is difficult to judge from transmission curves obtained photographically, the filament shows

a reddish tinge just prior to extinction which vitiates the comparisons.

Figure 2 gives the calibration curve for the measurement of the average particle size of carbon blacks with the microturbidimeter. The minimum extinction depth occurs for an average particle size of about 0.11μ , but this depends somewhat on the wave length of light used. It shifts toward a smaller value of the particle size for shorter wave lengths. The same phenomenon has been observed by Stutz (22) for suspensions of zinc oxide.

The curves in Figure 2 show that the count method of determining average particle size yields results which correlate well with the turbidity measurements in the sense that they are smooth curves. However, anomalous turbidimeter

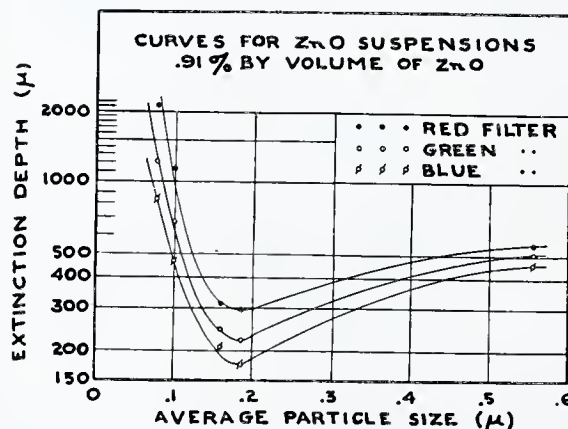


FIGURE 7

readings can be obtained by mixing blacks of widely different average particle size, so that the fact that smooth curves were obtained indicates that, in general, the carbon blacks had similar size-distribution curves.

Figure 3 shows the straight-line relation existing between the reciprocal of the concentration and the extinction depth for suspensions of P-33, with the different light filters used. In Figure 4, the line is extended to higher concentrations, the most concentrated cement used being 7.91 per cent by volume of black and having an extinction depth of only 28μ . The points in Figure 4 show a slight systematic deviation from a straight line, the curve bending toward the origin. For zinc oxide (see Figure 8), the linear relation holds all the way down to an extinction depth of about 30μ , corresponding to a concentration of 12.4 per cent by volume of zinc oxide. This was as high a concentration as could conveniently be obtained. It is interesting to compare these results with those previously reported for latex (7).

The dependence of turbidity on concentration for high concentrations and the appearance of a maximum such as occurs for latex is not well understood, although such maxima have been reported for other systems (16, 25).

Figure 5 shows an effect due to light absorption. For white pigments, such as zinc oxide or barium sulfate, and for latex, the extinction depth is practically independent of the filament intensity. For carbon black, however, there is a small dependence, the extinction depth being greater the brighter the filament. The effect is not extremely large, however, since the differences shown in Figure 5 were produced by a twelve-fold change in filament intensity. Measurements with color filters, for carbon black, have not taken account of differences in intensity of the transmitted light. This may explain why carbon black suspensions show better transmission with no filter than they do with a red filter, whereas the reverse is the case for zinc oxide (see Figures 3 and 8).

The turbidity of a suspension is dependent among other things on the difference in the index of refraction of the

two phases, so that in general a change in the index of refraction of the medium can be used to secure information about the index of refraction of the dispersed phase. It was thought that it would be interesting to do this for an absorbing dispersed phase such as carbon black.

For this purpose, additional suspensions of carbon black in carbon disulfide and in gasoline cements were prepared. For this range of the index of refraction, 1.489 to 1.617, the extinction depth showed no significant variation.

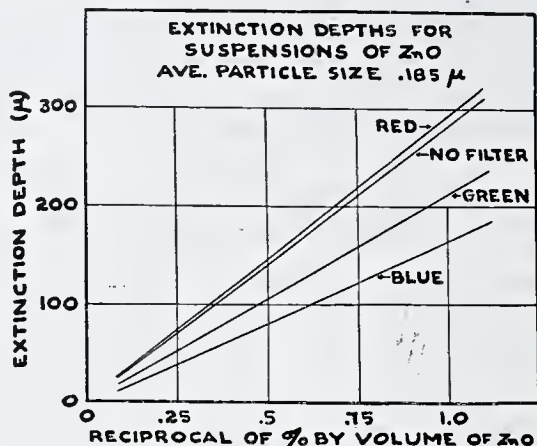


FIGURE 8

Figure 6 shows the effect of the index of refraction of the pigment on the extinction depth, giving the curve obtained by plotting the extinction depths for suspensions in xylene cement of barium sulfate, zinc oxide, and titanium oxide against their refractive indices which are respectively 1.64, 2.02, and 2.50.

In Figure 7 we have the calibration curves for the turbidimeter which make possible its use for measuring the average

size of zinc oxide pigments. If there is any question as to which side of the minimum the pigment belongs, it can usually be answered by taking readings with the red and with the blue filters. The ratio of these two readings is different on the two sides of the minimum.

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Volumetric Sulfate Determination

Rapid Method for Determining Sulfur in Organic Compounds

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DURING the course of some synthetic organic chemical reactions undertaken by one of the authors, it became necessary to follow the course of a reaction by means of sulfur determinations. To be of value, these determinations were of necessity very numerous, and for that reason a rapid volumetric method has been developed by means of which a complete determination may easily be completed within 30 minutes and as many as six completed within 1 hour.

Although the principles upon which the method is based are not new, the combination of oxidizing the organic compound in a Parr sulfur bomb followed by a sulfate determination with standard barium chloride, the excess of which is determined with sodium carbonate solution using phenolphthalein as an indicator, may be of value to other organic chemists. Three distinct advantages may be claimed for this method over other proposed volumetric methods: First, a minimum of operations is involved; second, no special reagents or apparatus other than a Parr sulfur bomb are required; and third, comparable and quantitative results are obtained in 30 minutes.

LITERATURE SURVEY

The determination of sulfur in organic compounds requires at least two steps: (1) conversion to inorganic sulfur, and

(2) determination of the inorganic sulfur. Two practicable means of converting organic sulfur into inorganic sulfur are available: reduction to hydrogen sulfide (6, 19, 21, 23), and oxidation to sulfate. At present, oxidation by means of sodium peroxide in a Parr sulfur bomb (26) is the most rapid and the most universally applicable method of obtaining the inorganic sulfur. The chief problem, therefore, lies in finding a rapid yet accurate means of determining the sulfate ion in the presence of a large excess of sodium chloride.

Determination of the sulfate ion may be based on the insolubility of silver (9), lead (24, 25, 38), benzidine (13, 16, 27, 28, 31), and barium sulfates, the least soluble being barium sulfate. Silver and lead, of course, form insoluble chlorides and cannot be used in the present case (38). Benzidine is not applicable in the presence of large quantities of any neutral salt (16). This leaves barium as the best suited for the purpose. Barium chromate (1, 14, 18, 29), phosphate (22), acetate (10, 15), hydroxide (35), and chloride have been used as precipitating agents. The most advantageous appears to be barium chloride since it forms stable solutions and is available in a very pure state.

Three methods are available for determining sulfate under these conditions: (1) photometric (32) determination of suspended barium sulfate; (2) gravimetric determination (11) of barium sulfate; and (3) volumetric determination of excess

standard barium chloride used in the precipitation. As rapid methods, the first and third are available.

Sodium chromate has been used to determine excess barium chloride (2, 5, 8, 12, 30, 34, 36). This method is undoubtedly accurate, but suffers the disadvantage of requiring an external indicator. Potassium palmitate has been suggested (3, 17, 37, 39), but suffers four disadvantages: (1) the standard reagent is an alcoholic solution; (2) only "purest palmitic acid" can be used; (3) preparation and standardization of the reagent are inconvenient; and (4) a factor must be subtracted from the titration value determined, thus making the error rather great at low sulfate concentrations (17).

The most promising reaction seemed to be embodied in the work of Vitali (33), as modified by Cooksey (7) and others (4, 20). The method depends upon precipitating barium sulfate with excess standard barium chloride solution. The excess barium chloride is determined in alcoholic solution by means of standard sodium carbonate using phenolphthalein as an indicator. The advantages of this method do not seem to have been appreciated during the last 24 years, and thus its outstanding advantage as a rapid yet accurate method of estimating sulfates, especially those prepared from organic sulfur compounds, should now be recognized.

PROCEDURE IN SULFUR DETERMINATION

Weigh to the nearest milligram 0.5 gram of the organic sulfur compound and transfer to the fusion cup of a Parr sulfur bomb.¹ Add 1 gram of potassium perchlorate and 15 grams of sodium peroxide. Seal the bomb and ignite in the usual manner. Cool the bomb under a cold-water tap, remove the cover and transfer the fusion cup to a 400-cc. beaker. Carefully wash any solid adhering to the cap into the beaker by means of a stream of water from a wash bottle. In this manner add not over 50 cc. of water, then cover the beaker with a watch glass and tilt by resting one side on a pencil so that the solid is extracted completely from the fusion cup. Solution will be complete by the time another sample has been weighed. Carefully rinse out the fusion cup with water and make the solution slightly acid to phenolphthalein by adding concentrated hydrochloric acid. Cover the beaker with a watch glass, place on a hot plate, and boil for approximately 10 minutes, or until all hydrogen peroxide has been decomposed and all carbon dioxide expelled. Make the solution just neutral to phenolphthalein using 0.2 *N* sodium hydroxide, and quickly filter through a small Büchner funnel using suction. This step eliminates the iron as hydroxide. A 500-cc. filter flask, moreover, is a convenient vessel in which to carry out the titration. Without cooling, add 100 cc. of No. 30 denatured alcohol (methanol may be used if desired, or 90 per cent grain alcohol, but not No. 5 or 24 denatured alcohol) and 25 cc. of 0.1 *N* barium chloride. Titrate the excess barium chloride with 0.1 *N* sodium carbonate to a faint but permanent pink end point. This titration should amount to at least 5 cc. of 0.1 *N* sodium carbonate solution.

$$(\text{cc. } 0.1 \text{ } N \text{ BaCl}_2 - \text{cc. } 0.1 \text{ } N \text{ Na}_2\text{CO}_3) \times 98 = \% \text{ H}_2\text{SO}_4$$

OBSERVATIONS

Special note has been made that the volume of aqueous solution be maintained at 50 cc. or less. This is desirable since the end point is almost instantly distinguishable in more concentrated solutions. As may be seen from Table I, this is probably a dilution effect which may be corrected by adding more alcohol, by heating, or both (4).

¹ For details of operation see book of instructions furnished by the Burgess-Parr Company, Moline, Ill., observing carefully the modifications here presented.

TABLE I. EFFECT OF ALCOHOL CONCENTRATION ON END POINT
(Commercial alcohol with denaturant No. 30 used)

ALCOHOL Cc.	WATER Cc.	0.1028 <i>N</i> BaCl ₂ Cc.	0.0494 <i>N</i> Na ₂ CO ₃ Cc.	ALCOHOL AT END POINT Vol. %	REMARKS
10	90	20.00	41.00	6	End point only slightly changed by boiling; very slowly attained (2)
20	80	20.00	41.50	12	Slow end point slightly changed by boiling
30	70	20.00	41.55	19	Slow end point corrected by heating at end point
40	60	20.00	41.60	25	Slow end point completed at room temperature
50	50	20.00	41.60	31	End point readily attained at room temperature
60	40	20.00	41.70	37	End point rapidly attained at room temperature
70	30	20.00	41.68	43	End point rapidly attained at room temperature
80	20	20.00	41.65	50	End point rapidly attained at room temperature
90	10	20.00	41.68	56	End point rapidly attained at room temperature
100	0	20.00	41.70	62	End point rapidly attained at room temperature

Sodium sulfate may be determined quantitatively by this method of titration, as may be seen from Table II. It would therefore seem possible to standardize the solutions against pure sodium sulfate. It is likewise possible to standardize the carbonate solution against pure potassium acid phthalate in the usual way, the ratio of carbonate to barium chloride solutions being determined in blank experiments.

TABLE II. TITRATION OF SODIUM SULFATE

Na ₂ SO ₄ SOLN. Cc.	ALCOHOL Cc.	0.1028 <i>N</i> BaCl ₂ Cc.	0.0494 <i>N</i> Na ₂ CO ₃ Cc.	Na ₂ SO ₄ FOUND Gram	Na ₂ SO ₄ CALCD. Gram
25	100	40.30	11.00	0.2574	0.2575
25	100	40.35	10.60	0.2578	0.2575
25	100	40.20	10.40	0.2574	0.2575
25	100	100.00	56.50	0.5310	0.5300
25	100	80.00	15.60	0.5300	0.5300
25	100	75.00	6.50	0.5256	0.5300

Sodium chloride seems to have very little if any effect on the end point attained in determining sodium sulfate, as may be seen from Table III.

TABLE III. EFFECT OF SODIUM CHLORIDE ON ESTIMATION OF SULFATE

Na ₂ SO ₄ SOLN. Cc.	NaCl ADDED Grams	ALCOHOL Cc.	0.1028 <i>N</i> BaCl ₂ Cc.	0.0494 <i>N</i> Na ₂ CO ₃ Cc.	Na ₂ SO ₄ FOUND Gram	Na ₂ SO ₄ CALCD. Gram
25	5	100	80.50	16.90	0.5286	0.5300
25	10	100	80.50	16.80	0.5288	0.5300
25	15	100	91.60	40.20	0.5277	0.5300

It is well to run blanks on the reagents used, especially the sodium peroxide and potassium perchlorate, as these contain appreciable quantities of sulfur unless the best commercial grades are obtained. A convenient manner of running a blank on the reagents is to burn 0.5 gram of pure benzoic acid in the bomb and continue the sulfur determination in the usual way.

Ferric iron introduced by corrosion of the fusion cup seems to have no detrimental effect when in the state of basic ferric acetate, other than to mask the end point slightly.

Either of two procedures, then, becomes possible at this point. As may be seen from Table IV, the addition of a few crystals of sodium acetate to the hot solution makes direct titration possible without any filtration. On the other hand, by making the solution faintly alkaline to phenolphthalein, the iron is precipitated as ferric hydroxide and may be removed by filtration. Using a small Büchner funnel and suction, the filtering operation is extremely simple and rapid. In Table V the first value for sulfur in *p*-toluenesulfonamide was determined after removing iron, and the second without filtering.

TABLE IV. EFFECT OF Fe^{+++} ON TITRATION VALUES

FeCl_3 AS 10% SOLN. Cc.	ALCO- HOL Cc.	0.1028 N BaCl_2 Cc.	0.0494 N Na_2CO_3 Cc.	RATIO Na_2CO_3 : BaCl_2	REMARKS
1	70	19.90	47.05	2.364	Neutral to phenolphthalein with NaOH
1	70	20.00	41.20	2.060	Neutral to phenolphthalein with NaOH + 0.2 g. NaOAc
1	70	20.00	41.85	2.092	Neutral to phenolphthalein with NaOH + 0.3 g. NaOAc
2	70	20.00	41.65	2.082	Neutral to phenolphthalein with NaOH + 2 g. NaOAc

Diluents other than No. 30 denatured alcohol have been tried. Acetone, 1-4, dioxane, No. 5 denatured alcohol, pyridine, and No. 24 denatured alcohol were all unsatisfactory, whereas methanol, 95 per cent grain alcohol, or No. 30 denatured alcohol proved equally satisfactory.

In order that some idea may be gained as to the accuracy of the results and the applicability of the method, Table V lists eleven substances which have been analyzed by two different analysts. These compounds represent extremes in sulfur content as well as in types of compounds which have been successfully analyzed by the method described.

TABLE V. RESULTS ON SEVERAL TYPES OF SULFUR COMPOUNDS
(Obtained by two analysts)

SUBSTANCE	SULFUR CALCD.		SULFUR FOUND	
	%	Analyst I %	Analyst II %	
Thiourea	42.12	42.30	42.28	
p-Toluenesulfonamide	18.72	18.60	18.66	
Diphenylsulfone	14.68	14.55	14.68	
Methyl orange (technical)	...	5.74	5.37, 5.33	
Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) ^a	12.83	12.83 12.80	12.72, 12.75	
Sodium sulfate (Na_2SO_4)	22.56		22.43, 22.50, 22.50	
Sulfanilic acid (anhydrous)	18.51	18.25	18.52	
Sodium o-benzoic acid sulfonide	14.49	14.45	14.52, 14.85	
Quinine sulfate	3.67	3.65	3.68	
Sulfonated oil (technical)	...	2.97, 2.92, 2.63	2.36, 2.34	
1-Amino, 2-naphthol, 4-sulfonic acid (commercial)	13.40	12.97	13.23	

^a Sample dissolved in water, slight excess NaOH added, boiled, filtered to remove copper, and titrated as above.

In summary it may be said that the method presented offers five advantages over the other titration methods which have been tried and which have come to the authors' attention. These advantages are: first, a minimum of operations; second, no special reagents; third, no special apparatus other than a Parr sulfur bomb; fourth, positive results obtainable in less than 30 minutes; and fifth, apparent applicability to all organic compounds which may be burned in a Parr sulfur bomb. Of course, it should be realized that phosphates,

arsenates, borates, and chromates which form insoluble barium salts will seriously interfere with the determination. Likewise, metals which form insoluble carbonates must be removed before the method becomes applicable.

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Thermostatic Control Operated by Ordinary Alternating Current

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A SIMPLE and effective circuit breaker operated by the commonly available 110-volt alternating current is preferable to any operated by batteries. H. S. Davis (2) has pointed out that the chemist may have overlooked the possibility of operating a relay by alternating current. A few such circuit breakers have recently been put on the market for use in temperature control. L. A. Richards (3) has described an adaptation of a commercial alternating current relay which is operated directly by the 110-volt source. Since the one developed can be made quite readily and since it has proved satisfactory for precise and extended temperature control for the past 3 years, its description may be of value to others.

The assembled circuit breaker is shown in Figure 1. A is an ordinary house-bell transformer, which reduces the 110-volt alternating current to 6, 12, and 18 volts, respectively. The electromagnet, B C D, is the clapper type, and is activated by a solenoid 1.125 inches (2.86 cm.) in diameter, with a 0.5-inch (1.27-cm.) core, and made of 3325 turns of No. 32 B. & S. cotton-covered copper wire. Such a solenoid may be obtained from any company carrying standard relay equipment. The armature C is supported at K by two 60-degree pivot bearings. The outer bearing is seated by means of a thumb screw and lock nut to permit the removal of the armature, if necessary, and the adjustment needed for free movement

without play. *E* and *F* are lengths of ordinary 0.5-inch (1.27-cm.) arc carbon, which are fitted into brass sleeves so that adjustment may be made as the carbon wears away. Contacts to the heating element are shown at *X* and *Y*. The external parts of the magnetic circuit (*C* and *D*) are made of ordinary mild steel 0.5 inch (1.27 cm.) square, although any

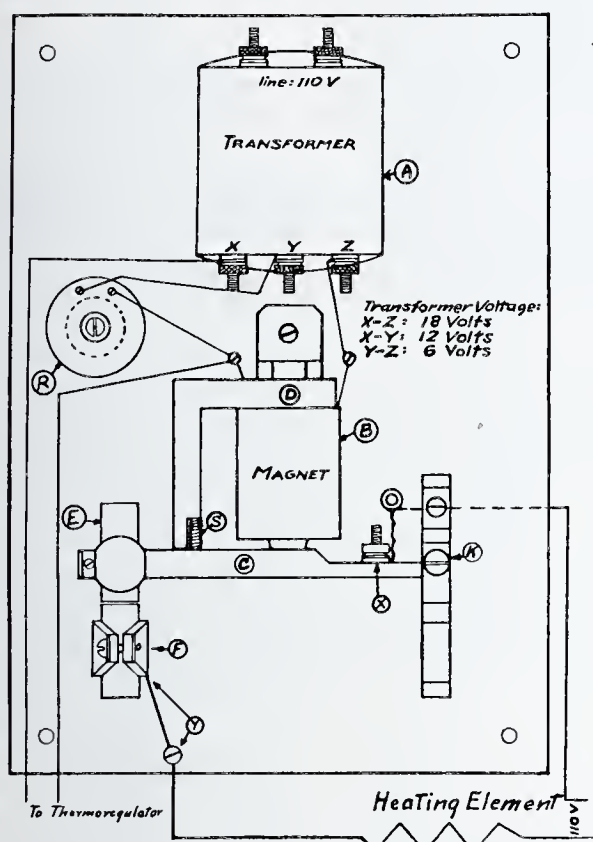


FIGURE 1. ASSEMBLED CIRCUIT BREAKER

steel or iron readily demagnetized would be as suitable. The shading coil, *S*, is made by splitting the pole piece *D* a distance of about 0.5 inch (1.27 cm.) and covering one half with copper wire (closed circuit) or with a copper band. This is the usual method of eliminating the clattering of pole pieces. If care is taken in fitting the armature with the other parts of the magnetic circuit, a shading coil is not necessary. The resistance, *R*, is approximately 200 ohms and may be conveniently made, as shown, in the form of a small coil of No. 36 B. & S. silk-covered "ideal" wire, or similar resistance wire. Since the amount of resistance required will vary somewhat with the material used in the magnetic circuit, a test is necessary in any particular case before obtaining a fixed resistance.

OPERATION OF CIRCUIT BREAKER

When the control circuit is closed by the expansion of the liquid, usually mercury or toluene, in the thermoregulator, 18 volts are applied to the solenoid *B*. This lifts the armature *C*, thus breaking the heating or power circuit. The current flowing in the control circuit is approximately 0.3 ampere, ranging from 0.2 to 0.4 ampere, in those in use at present. With this relatively large current in the control circuit, the weight of the armature used is sufficient to make the contact between the carbons as positive as necessary when the armature is released. The heaviest armature, including about 2 inches (5.08 cm.) of arc carbon, that has been used, weighs approximately 0.25 pound (0.11 kg.). However, considerably less weight than this is sufficient to prevent arcing at the carbon contact, even when the transite base to which the circuit breaker is attached is vibrated quite vigorously by an ordinary 0.25-horsepower motor attached to the same support.

The fact that the residual magnetism remaining after the

control circuit is broken in the regulator is sufficient most of the time to prevent the release of the armature, would, of course, eliminate the use of this device as a circuit breaker. It was found that this relatively large residual magnetism could be destroyed instantaneously by a small current, approximately 0.05 ampere, maintained through the solenoid by permanently applying 12 volts from the transformer through the resistance. This small current is not sufficient, however, to hold up the armature. The principle used here is somewhat similar to that applied in the demagnetization of a watch. The small alternating current is presumably capable of destroying a magnetization greater than it could itself establish. This, at least, was the theory which led to the use of this method.

The area of the surfaces of contact between the armature and the other parts of the magnetic circuit are diminished by cross-filing small grooves in the contact surfaces on *C* in order to eliminate the possibility of sticking due to the presence of oil or other like material.

The carbons, *E* and *F*, are not appreciably used up after a year of continuous use in opening and closing a heating circuit which consumes not less than 200 watts and at times as much as 400 watts. It is evident, from Figure 1, that their adjustment is very readily accomplished.

It was found best to make electrical contact with *C* at *X* and not through the pivot bearings at *K*, since slow corrosion of the bearings occurs owing to slight arcing. Permanent electrical contacts are soldered wherever loosening might occur.

ADVANTAGES

The following are the principal features which recommend this circuit breaker for thermostatic control.

1. The reliable 110-volt alternating current supply of electrical energy is used for both the heating and control circuits, thus avoiding the necessity of charging or replacing batteries and the danger of failure of the control while the power is on.
2. No springs are involved. The life of all parts is practically unlimited.
3. No fouling of power contacts is possible, since arc carbon is used. No condensers are required.
4. The space occupied is less than 0.5 square foot (464 sq. cm.). The circuit breaker may therefore be attached conveniently to the side of the thermostat.
5. The use of the transformer makes the control circuit quite independent of the heating or power circuit. The heating current may therefore be varied as required without affecting the control current.

THERMOREGULATOR REQUIRED

A thermoregulator in which electrical contact is made in an inert atmosphere, such as hydrogen or nitrogen, is needed with this circuit breaker; otherwise fouling at the contact would prevent precise and extended control. As pointed out by Wing (4), the magnitude of the control current is limited only by the volatilization of the mercury when contact occurs in an inert atmosphere. A very simple method of obtaining a permanent inert atmosphere is that described by W. Mansfield Clark (1). This method is applicable to most of the thermoregulators ordinarily used.

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CORRECTION. The title of the paper by R. C. Stratton, J. B. Ficklen, and W. A. Hough [*IND. ENG. CHEM., Anal. Ed.*, **4**, (1932)] reads "Calorimetric" in error for "Colorimetric Determination of Traces of Manganese and Chlorine with Benzidine."

Determination of True Temperature and Total Radiation from Luminous Gas Flames

Use of Special Two-Color Optical Pyrometer

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THE design of industrial furnaces to make proper utilization of the heat radiated from the flame and to provide adequate combustion space for the fuel is a field of engineering in which suitable methods of obtaining both the true flame temperature and its total emissivity are of obvious importance. This is particularly true in the design of luminous-flame furnaces, since the designer is so much more dependent upon empirical data on furnaces in actual operation than he is in predicting the performance of a furnace with nonluminous flame. The luminosity of a flame, caused by thermal decomposition of the hydrocarbon constituents of the fuel, is dependent in such a complex manner on excess air, type of mixing of air and fuel, air preheat temperature, and fuel composition, that any but an empirical treatment, based on test data, appears almost hopeless. A simple method of obtaining the most important of these data, true temperature and emissivity, is, therefore, highly desirable.

MEASUREMENT OF TRUE TEMPERATURE OF LUMINOUS FLAMES

Much work has been done on the development of methods for determining true flame temperatures.¹ These methods may be divided into two classes, those making use of a thermocouple, and those making use of photometry under conditions which eliminate errors due to flame transparency.

The first class is best known and has two subdivisions, in

¹ The question has been raised a number of times as to whether the term "true flame temperature" has any real meaning, since the term "temperature" is properly applicable only to a system in thermal equilibrium, with a certain distribution of energy among the various degrees of freedom of the system. Obviously, with combustion occurring in the flame, no such equilibrium exists. However, at the temperature levels attained in flames, the time required for a redistribution of energy, following a disturbing phenomenon such as combustion, may be safely calculated on the assumption that the equipartition principle is valid; and such a calculation indicates a period of the order of magnitude of 10^{-7} seconds. The fraction of the total flame body containing molecules which have not had a chance for redistribution of energy is consequently exceedingly small, and one may therefore use the term "temperature," as applied to a flame, with a high degree of exactness as to its meaning. Practically, the temperature of a flame may be defined as that attained by a small object, large compared to molecular diameters but small enough to acquire heat from the surrounding gases by convection and conduction much more readily than it can lose heat by radiation through the flame to the outside. It has been shown (16) that the soot particles in a luminous flame fulfil this requirement adequately, and attain a temperature differing from that of the surrounding gases by $+1^\circ\text{C}$.

This paper presents a proof of the possibility of determining both the true temperature and the total emissivity of a luminous flame from a pair of apparent temperatures obtained with an optical pyrometer, using color screens of two different effective wave lengths successively. The theory is tested experimentally on a series of one to six amyl acetate flames in a row. A pair of red and green brightness temperature readings should predict a true flame temperature independent of the number of flames through which the pyrometer is sighted. The actual average deviation from the mean of the six predicted true temperatures was only 4°C ., even though the brightness temperatures varied more than 200°C . for different flame thicknesses. The theory is further tested by calculating the total radiation from the flames and comparing the results with independent measurements of total radiation made with a narrow-angle thermopile replacing the optical pyrometer. The results indicate that the two-color pyrometer may be used to determine radiation from luminous flames with an average error of about 5 per cent.

the first of which the ratio of gas-convection coefficient of heat transfer at the couple to radiation coefficient is increased by one method or another. (a) In the so-called high-velocity thermocouple method, gas is drawn past the couple end at a high velocity, the couple reading being taken as equal to the gas temperature when a further increase in gas velocity has no effect. (b) The shielded couple is one so mounted that gas flows past it without obstruction, shields being placed around it in such a manner that it cannot "see" the cooler walls of the chamber. (c) The extrapolation method consists in the use of couples in varying size, with an extrapolation to zero couple diameter. This method is dependent on the effect of couple-end size on gas-film coefficient of heat transmission.

The methods in the second division use heat compensation.

(d) A couple is welded to a ribbon filament capable of being heated electrically, the whole being mounted as a high-velocity couple. When the filament heat is so adjusted that there is no difference in couple temperature with and without a flow of gas past the couple end, the couple is reading true gas temperature. (e) A wire of refractory metal is heated electrically *in vacuo*, and the relation between current and temperature is plotted. The latter is determined with an optical pyrometer and corrected for divergence from black-body conditions. The procedure is repeated with the wire in the flame. The point of intersection of the two curves corresponds to true flame temperature, for, since the flame is neither heating nor cooling the wire at this temperature, the radiation loss from the wire is the same as *in vacuo*.

The first four methods, requiring the use of bare thermocouples, are of little value for high-temperature or highly reducing flames. The fifth is restricted practically to laboratory use and, further, is inapplicable to luminous flames.

The various photometric methods of measuring true flame temperature are less applicable in plant work but sometimes of use in the laboratory. (a) If an optical pyrometer is sighted on a luminous flame and an auxiliary source of radiation of controllable brightness is placed behind the flame in the line of sight of the pyrometer, the latter can "see" the auxiliary radiator because of the partial transparency of the flame. The brightness temperature of the radiator, which may be a tungsten strip lamp, is adjusted until there is no difference between the reading of the optical pyrometer when

sighted directly on the radiator and when sighted through the flame onto it; the brightness temperature of the radiator is then the true flame temperature. The necessity for a controlled radiator in the line of sight of the flame makes this method impractical for plant use.

(b) When the flame is not luminous, the above method must be modified. The pyrometer is replaced by a spectroscopic, and the controlled radiator is viewed through the flame to which salt has been added. The NaD line is seen in the spectroscopic as a bright line or a reversed (dark) line, depending on whether the radiator has a brightness temperature above or below the true flame temperature. When the NaD line disappears, the radiator measures flame temperature. The radiator, which usually is not a true black body, must be calibrated for black-body brightness temperature at the wave length of the NaD line. The method, although excellent for laboratory flames, has obvious disadvantages for plant use.

(c) An apparent temperature is obtained by sighting through the luminous flame with an optical pyrometer, care being taken that the background in the line of sight is dark. A mirror is then placed in the line of sight and another apparent temperature determined, this time on a flame practically twice the effective thickness of the first. The application of the ordinary absorption law for monochromatic radiation, with allowance for reflection losses, permits a determination of true temperature from the two readings obtained. The equation to use is:

$$\left[1 - e^{-\frac{c_2}{\lambda} \left(\frac{1}{T_1} - \frac{1}{T}\right)}\right]^2 R = 1 - e^{-\frac{c_2}{\lambda} \left(\frac{1}{T_2} - \frac{1}{T}\right)}$$

in which c_2 is a constant of the Wien equation; λ is the mean effective wave length of the color screen in the pyrometer; T_1 and T_2 are apparent temperatures without and with the mirror in the line of sight of the pyrometer; R is the net reflectivity of the mirror for red light; and T is the desired true flame temperature.

In this and all subsequent equations, the reflectivity of flames is neglected. Ladenburg (13) and others (16) have shown this to be of the order of magnitude of 1 per cent.

THEORY OF TWO-COLOR METHOD

When an optical pyrometer is sighted on a non-black body to determine an apparent temperature or so-called red brightness temperature, T_R , the application of Wien's equation for the distribution of energy in the visible spectrum of a black body leads to the following equation relating red brightness temperature, T_R , true temperature, T , and monochromatic emissivity or black-body coefficient p_R :

$$\frac{1}{T_R} - \frac{1}{T} = -\frac{\lambda_R}{c_2} \log p_R \quad (1)$$

The term λ_R is the effective wave length transmitted by the red screen in the pyrometer. This is the expression generally used for correcting the observed temperature when the red emissivity p_R is known (5). If the object sighted on is a luminous flame, the red emissivity may vary between zero and unity as the flame thickness increases, and one must inquire further into the relation existing among p_λ , λ , and flame thickness. The emissivity of a flame is numerically equal to its absorptivity—i.e., to the fraction of a beam, incident on the surface of a flame, which is absorbed on passage through the flame. The monochromatic absorptivity A_λ of a diathermanous medium is given by the absorption law,

$$A_\lambda = 1 - e^{-k_\lambda L} \quad (2)$$

in which L is thickness and k_λ a constant called the absorption coefficient. The latter is dependent upon the wave length

of the radiation, and a convenient mathematical form for this dependence, valid over a limited wave-length range, is:

$$k_\lambda = k/\lambda^\alpha \quad (3)$$

in which α is a constant (for the limited wave-length range). This relationship will be further discussed later. From Equations 2 and 3 and the equivalence of A_λ and p_λ , the monochromatic emissivity of a flame is given by:

$$p_\lambda = 1 - e^{-kL/\lambda^\alpha} \quad (4)$$

Schack (16) has pointed out that, knowing α and λ , one could combine Equations 1 and 4 to solve for the product term kL , if both T_R and T were experimentally determined by the use of an optical pyrometer and a high-velocity thermocouple, respectively. Knowing kL and the law of variation of

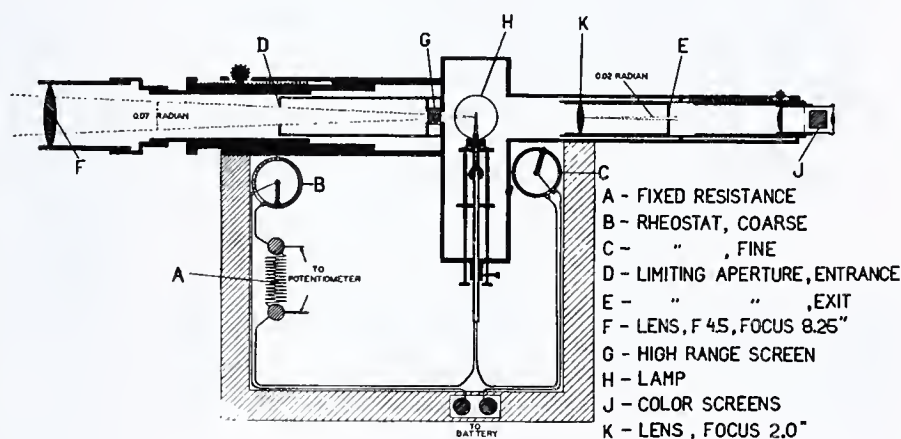


FIGURE 1. OPTICAL PYROMETER

emissivity with wave length, one could then combine the Planck equation for black-body radiation with Equation 4, integrate, and determine the total radiation from the flame per unit of area of its envelope. The objection to the method, pointed out by Schack himself, is the necessity for using unreliable high-velocity thermocouples in luminous flames, and the dependency of the accuracy of the method on the difference of two temperatures usually fairly close together and obtained with two entirely different types of instruments.

An inspection of Equations 1 and 4 indicates another possibility, however. Substituting the value for monochromatic emissivity p_R from Equation 4 in Equation 1, one obtains the relationship,

$$\frac{1}{T_R} - \frac{1}{T} = -\frac{\lambda_R}{c_2} \log \left(1 - e^{-kL/\lambda_R^\alpha}\right) \quad (5)$$

If the color screen in the pyrometer is changed from red to, say, green, and the flame's green brightness temperature T_G is determined, an equation similar to Equation 5 may be written with the subscript G replacing R throughout.

$$\frac{1}{T_G} - \frac{1}{T} = -\frac{\lambda_G}{c_2} \log \left(1 - e^{-kL/\lambda_G^\alpha}\right) \quad (6)$$

If the effective wave lengths λ_R and λ_G and the constants c_2 and α are known, and the red and green brightness temperatures T_R and T_G are measured, there are then but two unknowns in Equations 5 and 6, T and kL . A solution is therefore possible, yielding the desired true flame temperature and the term kL , which will be called the absorption strength of the flame. The total emissivity of the flame may then be evaluated readily. It is given by

$$p = \frac{\int_0^\alpha p_\lambda \cdot E_\lambda \cdot d\lambda}{\sigma T^4} \quad (7)$$

in which p is the desired total emissivity; E_λ is the monochromatic emissive power of a black body given by the Planck equation; p_λ is the monochromatic emissivity given in terms of wave length and known absorption strength, kL , by Equation 4; and the denominator σT^4 is the total radiation from a black body as calculated by the Stefan-Boltzmann equation.

The testing of the practicability of using Equations 5, 6, and 7 to determine true flame temperature and total emissivity involves the construction and calibration of an optical pyrometer with color screens of two different effective wave lengths,

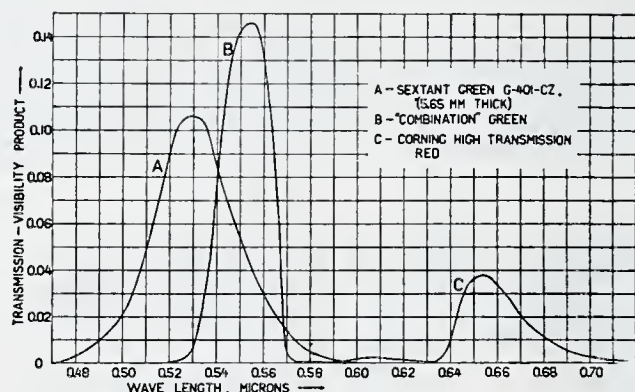


FIGURE 2. TRANSMISSION-VISIBILITY CURVES FOR THREE COLOR SCREENS

the accurate determination of those wave lengths, and the construction of burners capable of giving steady and duplicable luminous flames, on which measurements may be made of red and green brightness temperature, true temperature, and total radiation.

DESCRIPTION OF PYROMETER

The familiar disappearing-filament type of optical pyrometer, depending on the match of brightness of light of a certain color from a tungsten filament against that from the object sighted on, was chosen for use because of the high precision obtainable in this type of instrument when proper precautions are taken. In the early work on the problem a modified Leeds and Northrup plant type of instrument was used, but this was later replaced by an instrument of much higher precision, built after the specifications of the Bureau of Standards instrument described by Fairchild and Hoover (3). The color screens were placed in the Huygens eyepiece, in a slide permitting easy interchange of red and green screens. Figure 1 is a semi-diagrammatic representation of the instrument. The special features differentiating it from the familiar plant-type pyrometer are a fixed entrance aperture of 0.07 radians, a fixed exit aperture of 0.02 radians obtained by placing a diaphragm behind lens K at a distance equal to the focal length of the lens, a ball-and-socket adjustment for the lamp, object magnification of unity at a working distance of 16 inches (40.6 cm.) from object to object lens, variable filament magnification of about 20, and the use of a potentiometer instead of a millimeter to measure lamp current.

The procuring of suitable color screens presented a problem on which considerable time was spent. Inasmuch as the wave lengths of the light used for determining the brightness temperatures of the flame enter into Equations 5 and 6 used for calculating true flame temperature from the red and green brightness temperatures, it is essential to know those wave lengths. Since any glass color screen transmits light over a considerable range of the visible spectrum, it is necessary in making optical pyrometric calculations to use the so-called "effective" wave length (4), which varies slightly with the color temperature of the object sighted on. In the present work it is particularly desirable to minimize this variation in order to treat the wave-length terms λ_R and λ_G in Equations 5 and 6 as known constants. The extensive develop-

ment work on optical pyrometry using red light has yielded a red screen entirely satisfactory from the standpoint of insensitivity of its effective wave length to changes in color temperature of the object sighted on. Green screens, however, have not been much used in pyrometric work, and it was consequently necessary to find a combination of glasses which transmitted a sufficiently narrow band of light in the green range of the spectrum. Transmission curves of various available glasses and gelatin filters were studied, and combinations calculated and then examined experimentally with a spectrophotometer. A combination of glasses with a gelatin filter showed desirable transmission characteristics but was discarded because of the lack of permanence of the transmission characteristics of gelatin filters. After other combinations had been tried, a screen was finally chosen composed of the following glasses cemented together:

Corning corex green A	5.10 mm. thick
Corning yellow G-34y	1.02 mm. thick
Corning didymium G-555P	5.44 mm. thick

The criterion of insensitivity of effective wave length to changes in temperature of the object sighted on is the narrowness of the hump in the curve obtained by plotting, against wave length, the product of the per cent transmission by the visibility of the human eye. Such curves are presented in Figure 2 for the red screen, the green screen combination mentioned above, and a "sextant green" screen (7) sometimes used in pyrometry and ordinarily considered fairly monochromatic. The transmission curves for the two screens used were determined at wave-length intervals of 0.005 to 0.010 μ by the Bureau of Standards; the visibility curve of the average eye was taken from the paper of Gibson and Tyndall (6). The combination green screen is an obvious improvement over the single glass and a necessary step in the solution of the special problem on which it is used.

The calculations of effective wave length of the two color screens by the method outlined by Foote (4) may be summarized by the following equations:

$$1/\lambda_R = 1.5145 - \frac{19.8}{T} \quad (8)$$

$$1/\lambda_G = 1.8229 - \frac{40.2}{T} \quad (9)$$

T is the color temperature of the object sighted upon. These equations may be used directly for determining the effective wave length to use in Equations 5 and 6, when the optical pyrometer is used without any high-range absorbing screen. When such a screen is used, however, a "mean effective" wave length, λ'_m , must be used (4), defined in terms of effective wave length, λ_m , apparent or low-range temperature, S , and color temperature, T , by the equation

$$\frac{1}{\lambda'_m} = \frac{\int_{1/S}^{1/T} \frac{d(1/T)}{1/T - 1/S}}{\frac{1}{T} - \frac{1}{S}} \quad (10)$$

If the variation of effective wave length λ_m with color temperature T is of the type expressed by Equations 8 and 9 an integration of Equation 10 shows that Equation 8 or 9 may be used directly to obtain the mean effective wave length, if for temperature T there is substituted the harmonic mean of color temperature and the low-range temperature.

The optical pyrometer was calibrated with the red screen by comparison with a standard wide-ribbon tungsten lamp calibrated at the General Electric Nela Park Research Laboratory, which furnished a five-point calibration² of red brightness

² The temperature scale was based on the melting point of gold equal to 1336° K., and the constant C_2 of the Wien equation equal to 1.433 cm. degrees. In the temperature range of the present work, this scale differs by no more than 0.5° from the International Temperature Scale with $C_2 = 1.432$.

temperature *vs.* amperes. A cubic equation was fitted to these data by the method of least squares. The ribbon lamp could not be used directly for calibration of the pyrometer with the green screen since the tungsten ribbon is not a black body. In theory it is possible to calculate the green brightness temperature of tungsten from its red brightness temperature if its emissivity is known. However, since the data of Worthing (20) and Henning and Heuse (9) on the monochromatic emissivity of tungsten are not in agreement as to the effects of temperature and of wave length, it seemed preferable to calibrate directly by sighting on a black body with red and green screens alternating, the reading with the already calibrated red screen serving to determine the temperature of the object. The black body consisted of a silica tube closed at one end and inserted into an electric furnace. The tube was coated inside with chromium oxide, which has a high emissivity, and in addition was provided with stops to approach more closely theoretical black-body conditions.

As an independent basis of calibration of the red screen, the fusion temperature of copper was determined. The pyrometer as calibrated with the N. E. L. A. lamp indicated a melting point of 1082° K., as compared to the true melting point of 1083° K.

To extend the scale of the pyrometer, an absorbing screen was used consisting of 0.302 cm. of Corning blue-green C-171-IZ and 0.164 cm. of Corning purple glass G-555-CP. This particular combination of thicknesses was chosen because it had the same effective transmissivity of about 9.5 per cent for both the red and the green.

EXPERIMENTAL FLAMES

Inasmuch as the objects of this work were to demonstrate the practicability of the double-screen pyrometer as an instrument for determining true flame temperature and emissivity, and to determine a constant to be used in the calculations, it was essential that flames of controlled thickness and constant temperature be used. If a number of luminous flames, all exactly similar in height and luminosity, are arranged in a straight row, with provision to move as many of them as desired out of the straight line, the pyrometer may be sighted through flame of any thickness corresponding to multiples of the thickness of a single flame. The true flame temperature as obtained from the pyrometer readings should be the same regardless of the number of flames sighted through. In addition, a suitable analysis of the brightness temperature readings should permit a determination of the desired constant α of Equation 3.

The experimental flames first used consisted of a row of twelve single-jet gas burners, the brass tips being provided with 0.02 by 0.962 inch (0.05 by 2.44 cm.) passageways uniformly sized to insure uniformity of flames. The main gas manifold was fed from a constant-pressure regulator. Instead of the various flames being moved into or out of the line of sight of the optical pyrometer, a thin sheet-iron plate coated with soot was used to cut off vision of the flames not desired. Although this arrangement was carefully made, it was unsatisfactory on account of the imperfect alignment of the flames and their insufficient diameter.

The second set of experimental burners was considerably more elaborate, and consisted of a row of six amyl acetate lamps made substantially in accordance with the specifications of the Hefner standard lamp used in photometry with the exception of the material used in the construction of the wick tube. The lamps were adjusted with sight tubes to control the heights of the flames accurately to the standard 40 mm., and were mounted on slides to permit their being moved into or out of the line of sight of the pyrometer. To lessen trouble from flickering, each lamp was provided with a 200-mesh

copper-gauze chimney, perforated around its base and provided with two 0.25-inch (0.63-cm.) holes in the line of sight of the pyrometer, 22 mm. above the tops of the wick tubes. The chimneys were adequate to eliminate flicker due to air currents in the room and because of their porosity they did not produce sufficient stack effect to distort the flames excessively.

DATA AND RESULTS

The readings were made on different combinations of the six lamps to give the desired flame thicknesses. All six were used separately for the single flame-thickness readings, whereas only one combination was possible for the six flame-thickness measurement. Ten pairs of readings with the pyrometer were averaged for each combination tried. Table I shows the average of the ten temperatures obtained with each combination of lamps.

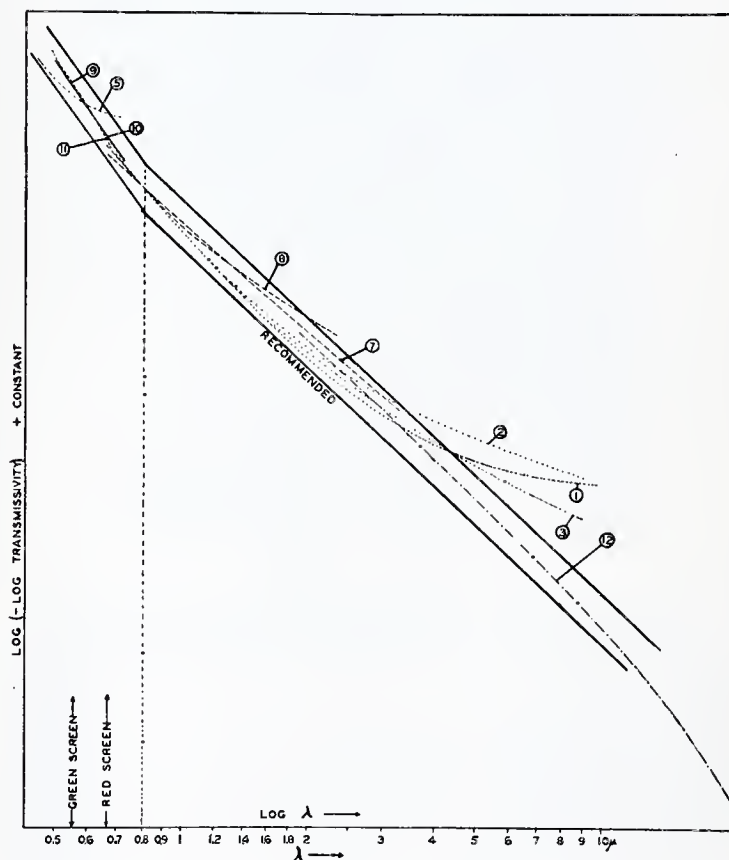


FIGURE 3. TRANSMISSIVITY DATA OF VARIOUS INVESTIGATORS ON SOOT LAYERS AND FLAMES. Wave lengths, from 0.5 to 20.0 microns

1. Ångström, stearin soot, 0.009 mm.
2. Ångström, stearin soot, 0.023 mm.
3. Ångström, stearin soot, 0.038 mm.
5. Stark, gas soot, av. of 6 sets of data on layers 0.010 to 0.016 mm.
7. Ladenburg, amyl acetate flame
8. Ladenburg, acetylene flame
9. Becker, amyl acetate soot, thinnest layer
10. Becker, amyl acetate and turpentine soots, av. of 12 sets of data
11. Becker, amyl acetate flame
12. Rubens and Wood, stearin soot, 0.0326 mm.

It will be noticed (Table I) that the average reading of a particular group of lamps differs very little from the average of all arrangements having the same total number of flames. Since each flame was used in at least one combination, it may be concluded that the flames cannot have differed much from one another.

The first analysis of the data of Table I was to determine the true temperature of the flame independently of the theory of the two-screen method. Equation 5 may be rewritten as

$$\frac{1}{T_R} - \frac{1}{T} = -\frac{\lambda_R}{c_2} \log \left(1 - e^{-nkL/\lambda_R^\alpha} \right) \quad (11)$$

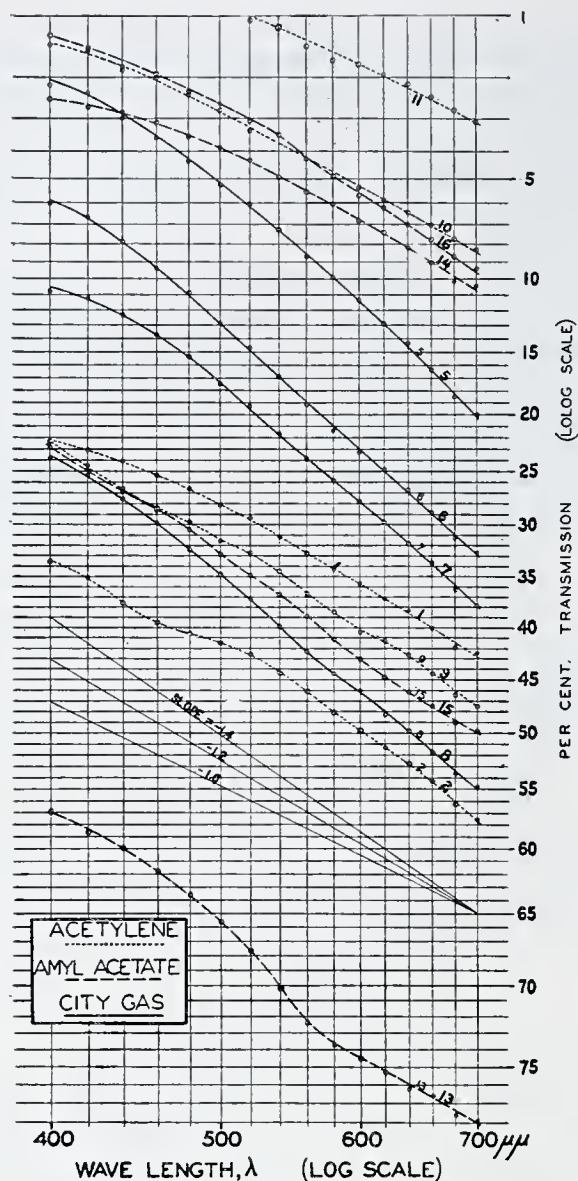


FIGURE 4. TRANSMISSIVITY DATA ON SOOT LAYERS OF VARYING THICKNESSES AND SOURCES

in which kL is the absorption strength of one flame and n is the number of flames sighted through. The term kL/λ_R^α will then be a constant for all the red brightness-temperature readings of Table I. If readings are obtained with the red screen for two different values of n , there will be two equations of the type of Equation 11, with true temperature T and kL/λ_R^α as unknowns. A preferable method of analysis, in which all the red data of Table I are used instead of just two points, becomes apparent when Equation 11 is rewritten in the form

$$\log \left[-\log \left(1 - e^{\frac{c_2}{\lambda_R} \left(\frac{T - T_R}{T \times T_R} \right)} \right) \right] = \log n + \log [kL/\lambda_R^\alpha] \quad (11a)$$

If one knows the true flame temperature T , a straight line with unit slope will be obtained by plotting the left side of the equation against $\log n$. The true value of T can therefore be found by assuming a number of values for T and determining that value which will give a straight line of unit slope when the data are plotted as described. The slope rather than the straightness of the line is found to be the better criterion of proper choice of T .

This method of analysis of the red brightness-temperature data for $n = 1$ to 6 yielded a value for true flame temperature of 1698.5°K . A similar analysis of the green data led to a value of 1690.8°K . The average of these is 1694.7°K . Subsequent calculations indicated that the groups of data for two and for

six flames in a row did not correspond to the same true flame temperature as the other four groups, possibly because of a temporary change in humidity of the air with a corresponding change in flame temperature. The data for $n = 1, 3, 4, 5$ yielded true temperatures of 1695.7° and 1694.0°K . for the red and green data, respectively, the average being 1694.9°K . It should be noted that these two temperatures, so close together, are obtained independently of any assumption of validity of the two-screen theory.

Ladenburg's (13) determination of the true temperature of the standard Hefner lamp was 1704°K ., with a possible error of 0.015μ in the wave length of his pyrometer, which would introduce an error of $\pm 8^\circ$ to 10° . Kurlbaum's (12) average of six determinations was 1704°K ., with an average deviation of each of 8° and a maximum deviation of 17° . Becker (2) calculated a probable temperature of 1670°K . based on data of Ångström and Leder.

TABLE I. OPTICAL PYROMETER READINGS ON FLAMES

NO. OF FLAMES IN ROW	BURNER NOS. USED IN COMBINATION	AV. OF TEN READINGS		AV. OF GROUPS		MAX. DEVN. OF ANY BURNER GROUP FROM AV.	
		$T_R^\circ \text{K.}$	$T_G^\circ \text{K.}$	$T_R^\circ \text{K.}$	$T_G^\circ \text{K.}$	$T_R^\circ \text{K.}$	$T_G^\circ \text{K.}$
1	1	1472	1524				
	2	1478	1530				
	3	1476	1527	1475	1528	3	4
	4	1477	1530				
	5	1475	1526				
	6	1476	1529				
2	1, 2	1536	1581				
	3, 4	1536	1582	1536	1582	1	1
	5, 6	1537	1583				
	4, 6	1536	1582				
	1, 3	1535	1581				
3	1, 2, 3	1582	1619				
	2, 4, 6	1581	1618	1583	1619	2	2
	4, 5, 6	1585	1620				
	1, 3, 5	1582	1619				
4	1, 2, 5, 6	1598	1630				
	1, 2, 4, 6	1599	1633	1600	1632	2	3
	1, 3, 5, 6	1598	1631				
	2, 3, 4, 5	1601	1635				
5	1, 2, 3, 5, 6	1619	1647				
	2, 3, 4, 5, 6	1623	1650	1621	1649	2	2
6	1, 2, 3, 4, 5, 6	1635	1656	1635	1656	.	.

These values are not strictly comparable to the present determination, since the present lamps were not standard in the important detail of wick-holder metal and thickness which would affect the rate of heat transfer into the wick, consequently the volatilization rate of the amyl acetate, and thus the diameter and temperature of the flame.

DETERMINATION OF α

The use of the two-color principle necessitates a knowledge of the value of α , the exponent on wave length in the equation of variation of absorption coefficient with wave length. In using Equation 11a to determine T from the red data, one obtains also the value $\log (kL/\lambda_R^\alpha)$ as the intercept of the straight line. Similarly, $\log (kL/\lambda_G^\alpha)$ is obtained from the green data. The difference of these two terms equals $\alpha \log (\frac{\lambda_G}{\lambda_R})$ from which knowing λ_G and λ_R , one may find α . For the data corresponding to $n = 1, 3, 4, 5$, α is found to be 1.39.

Independent data of other investigators on the transmissivity of flames and soot layers are available for determining α . The transmissivity Tr of a flame equals one minus its absorptivity, and since the latter equals emissivity p , it follows from Equation 4 that

$$Tr = e^{-kL/\lambda^\alpha} \quad (12)$$

$$\text{or} \quad \log (-\log Tr) = \log kL - \alpha \log \lambda \quad (12a)$$

If this relationship is valid, a plotting of $\log (-\log Tr)$ against $\log \lambda$ should produce a straight line with a slope of $-\alpha$, and

flames of different thicknesses should correspond to lines of the same slope but displaced up or down according to the value of the constant $\log kL$ of Equation 12a. In Figure 3 the data of various investigators are shown plotted in this way, with the lines displaced up or down to compensate for differences in thickness of the absorber and to produce substantial superimposition of the lines. The discussion for the present is concerned only with the left side of the figure, in the wave-length range from green to red. The heavy lines boxing in the curves have the slope -1.39 corresponding to the value of α determined with the two-color pyrometer in the present investigation. Becker's data (2) on the amyl acetate flame and on amyl acetate and turpentine soot are seen to be in excellent agreement, corresponding to an α of about 1.4. Stark (19), however, ten years previously, had obtained data on gas soot (Curve 5) which indicate an α of about 0.5 in the green to red range.

Although the infra-red measurements of Ångström (1), Ladenburg (13), and Rubens and Wood (15) indicate that Becker's results are more reasonable than Stark's, it seemed desirable to make some additional determinations of transmissivities of soot layers from different sources. Accordingly soot layers of different thicknesses were deposited on microscope cover glasses from the flames of a luminous gas jet burning Cambridge city gas, acetylene, and amyl acetate successively. Spectrophotometric-transmission curves were determined, and are presented in Figure 4, in which $\log (-\log Tr)$ is plotted against $\log \lambda$. It will be noted that the data included layers with transmissivities varying from 1 to 78 per cent. Figure 5 shows the curves moved up or down to superimpose them in three groups according to the source of the soot. The average values of α for amyl acetate soot, acetylene soot, and illuminating gas soot are 1.30, 1.23, and 1.75, respectively, in much better agreement with Becker's data than with Stark's. Inasmuch as the mechanism of cutting down the intensity of a beam passing through a turbid medium is one not so much of true absorption as of dispersion, one may expect the variation of absorption coefficient with wave length to be a function of particle size, and consequently not the same for flames as for soot deposited from them, or even for different flames or different soots. The individual variations of α shown in Figure 5 for acetylene soot, for example, may be due to production of soot at different temperatures due to the successive microscope cover glasses being held in different parts of the flame. The data of Figures 3, 4, and 5 indicate, however, that the probable deviation of α from the value of 1.39 fixed by the two-screen pyrometer with an amyl acetate flame, will not exceed 20 per cent. The effect of such a deviation will be discussed later.

APPLICATION OF TWO-SCREEN METHOD TO TRUE-TEMPERATURE DETERMINATION

With α fixed at 1.39, it is now possible to test the two-screen theory by putting pairs of values of red and green brightness temperatures, for different values of n , into Equations 5 and 6, and solving for T and kL . Constant values for mean effective wave lengths of the color screens of 0.6651μ and 0.5553μ were used for the red and green, respectively.³ The results of the calculations are presented in Table II, which shows the value of T , the true temperature, calculated from each pair of values of T_R and T_G . The average of the true temperatures so calculated is 1695.2°K. , and the deviation of each value from the average is given in the last column. It will be noticed that

³ Although λ_R and λ_G vary in accordance with Equations 8, 9, and 10, the variation over the range of the present experimental work was small, and was, furthermore, of the same order of magnitude for both screens. λ_R varied 0.14, and λ_G 0.22 per cent, but their ratio varied only 0.07 and their difference 0.24 per cent.

the average value is extremely close to the value already determined independently of the two-screen method, 1694.9°K. , and that the deviations from the average are quite small in four out of the six cases. The reason for the deviations for two and six flames in a row is unknown. The possible change in humidity of the air has already been suggested as the explanation, though there is no possibility of proving this to have been the true cause. The deviations are believed to be outside the limit of experimental error and to represent real

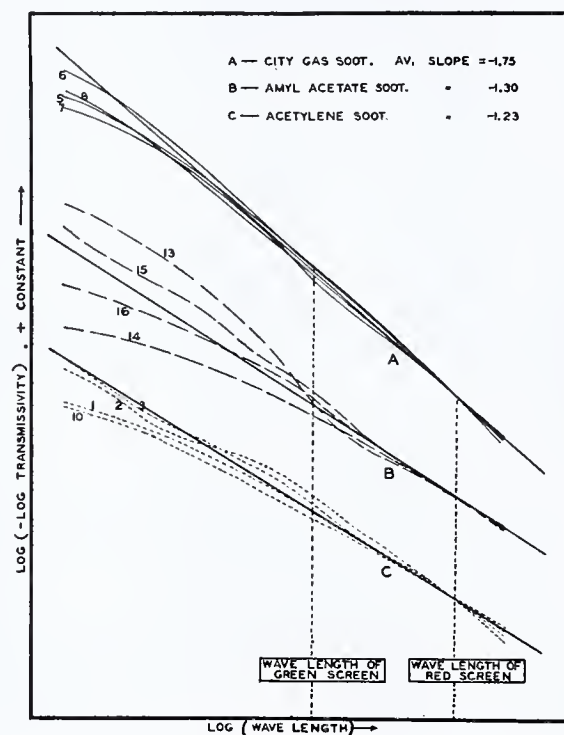


FIGURE 5. TRANSMISSIVITY DATA FROM FIGURE 4 ARRANGED ACCORDING TO ORIGIN OF SOOT

differences in true flame temperature. Even granting them to be experimental error, the average deviation is only 4° , establishing quite satisfactorily the validity of the two-screen method for measuring the true temperature of a luminous flame.

Inasmuch as there is some uncertainty as to the proper value of α and a possibility of its having a different value for luminous flames of other fuel source, calculations were made to determine how much error would be introduced by the use of other values for it. The results are given in Table III. It is seen that for moderately thick flames (equal in density to six times the thickness of a single Hefner flame) the error due to α 's changing to as much as 1.7 from 1.39 is only 7.6°K. If α varies no more than from 1.36 to 1.42, the error even on a single flame thickness is but 2° owing to the use of a constant value of 1.39 for α .

TABLE II. SUMMARY OF TRUE-TEMPERATURE CALCULATIONS

NO. OF FLAMES	T_R $^\circ \text{K.}$	T_G $^\circ \text{K.}$	T $^\circ \text{K.}$	DEVN. FROM AV. $^\circ \text{K.}$
1	1475	1528	1696.3	+ 1.1
2	1536	1582	1704.6	+ 9.4
3	1583	1619	1695.5	+ 0.3
4	1600	1632	1693.1	- 2.1
5	1621	1649	1696.8	+ 1.6
6	1635	1656	1684.9	-10.3
∞	1695.7	1694.0		
			Av. 1694.9	
			Av. 1695.2	

Inasmuch as the use of Equations 5 and 6 to determine temperature and absorption strength is extremely tedious, involving trial and error, a working plot is presented in

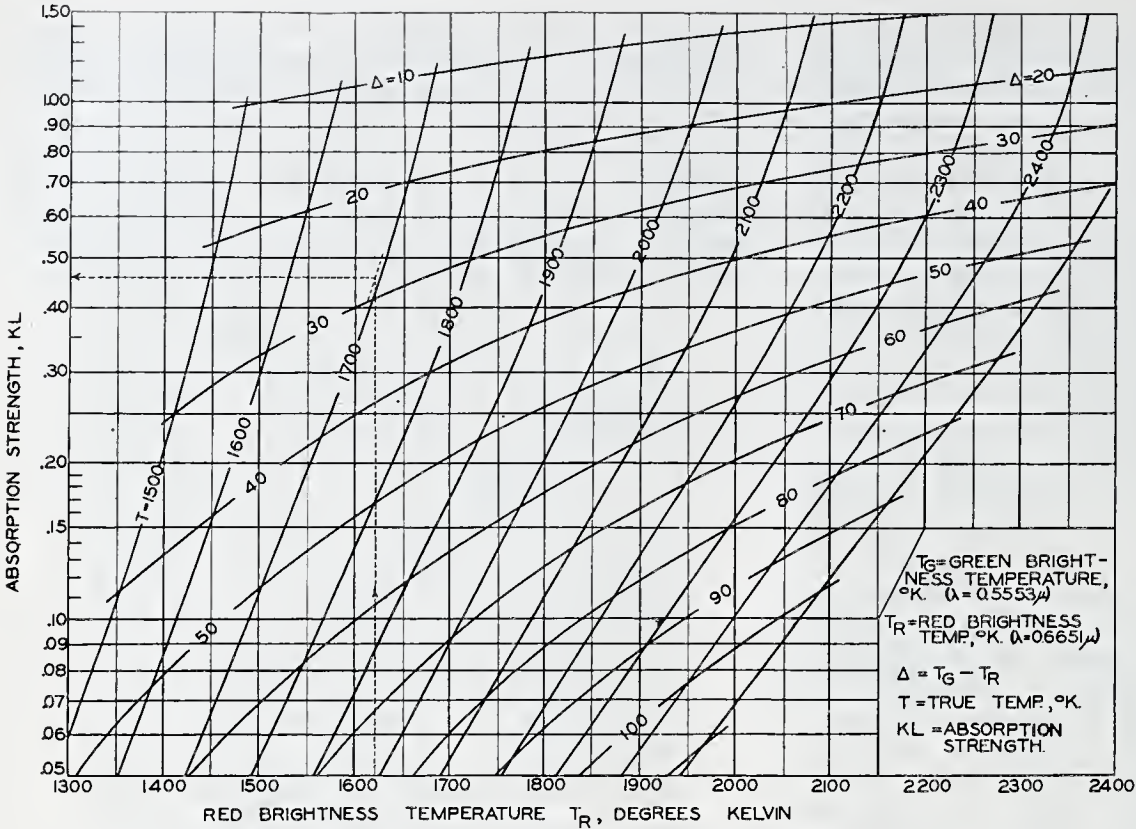


FIGURE 6. TRUE TEMPERATURE AND ABSORPTION STRENGTH OF LUMINOUS FLAMES
As functions of red and green brightness temperatures

Figure 6 to permit a ready determination of the desired quantities as soon as one has determined T_R and T_G experimentally. From the value of T_R on the abscissa one goes vertically to the proper value of $(T_G - T_R)$, then reads true temperature T by interpolation on the semi-vertical lines, and kL on the ordinate.

TABLE III. ERROR IN TRUE-TEMPERATURE CALCULATION DUE TO ERROR IN α
(True α assumed, 1.39)

No. OF FLAMES	$\alpha = 1.36$ ° K.	$\alpha = 1.42$ ° K.	$\alpha = 1.50$ ° K.	$\alpha = 1.70$ ° K.
1	+2.3	-1.9	-8.8	-27.7
2	+2.0	-1.8		
3	+1.7	-1.7		
4	+1.2	-1.3		
5	+1.0	-1.2		
6	+0.9	-0.8	-3.4	-7.6

APPLICATION TO DETERMINATION OF TOTAL EMISSIVITY

With the true flame temperature shown to be determinable, it was desired further to test the theory and the instrument by comparing the total calculated radiation with actual measurements made with a total-radiation thermocouple. According to Equation 7, the total emissivity is

$$p = \frac{\int p_{\lambda} \cdot E_{\lambda} \cdot d\lambda}{\sigma T^4}$$

The monochromatic emissivity p_{λ} has been shown to be adequately represented by $(1 - e^{-kL/\lambda^{1.39}})$ in the green to red range of the spectrum, but a study of Figure 3 shows that α becomes less as one passes further into the infra-red. Schack (16) suggested that two values of α were adequate to represent the complete range of the spectrum in which one is interested for heat-transfer calculations. On inspecting the data represented in Figure 3, it was decided that a value of α of 1.39 out to $\lambda = 0.8\mu$, and of 0.95 from 0.8μ to 10μ would adequately represent the variation of p_{λ} with wave length. (The works of Rubens and Wood (15) should receive more weight than that of the other investigators in determining a proper value for α in the infra-red.) The evaluation of total

emissivity from Equation 7 was performed graphically for various values of T and kL , the results being presented in Figure 7, which is self-explanatory.

The calculation of the total radiation from a flame (due to its luminosity) consists in reading true temperature and absorption strength from Figure 6 when T_R and T_G are known, then reading total emissivity p from Figure 7, and multiplying the latter by the radiation from a black body at the true temperature T , as given by the Stefan-Boltzmann equation. Results of this type are presented for one, two, and three Hefner flames in a row in Table IV. In addition to the radiation due to flame luminosity, however, there is some non-luminous gas radiation, small but not negligible. This may be calculated if one knows the flame thickness, the percentage

carbon dioxide and water vapor in it, and its temperature (11). Since only the last of these is known with accuracy, any calculation of this type must of necessity be very rough. Table IV also shows the estimated gas radiation added to the radiation due to soot luminosity. Although the total radiation due to the two mechanisms is somewhat less than the sum of the two effects individually calculated, the necessary roughness of the nonluminous radiation calculation does not merit any such refinement in combining the two effects.

TABLE IV. TOTAL RADIATION FROM FLAMES

No. OF FLAMES IN ROW	(a) RADIATION DUE TO LUMINOSITY CALCD. FROM T_R AND T_G	(b) COL. (a) PLUS ESTIMATED NON-LUMINOUS GAS RADIATION	(c) TOTAL RADIATION MEASURED WITH THERMOPILE	DIFF. (c) - (b) (c) × 100
				%
1	7060	8760	8220	-6.6
2	12400	14930	15560	+4.05
3	20930	23960	22270	-7.6

The comparison of the above calculated results with experiment was made by C. H. Gilmour, who determined the total radiation from one, two, and three flames in a row with a narrow-angle thermopile of two junctions of bismuth-tin and bismuth-antimony wire. The receiving surfaces of the pile, to which the alternate junctions were fastened, formed a circular disk having a diameter of 1 mm. and lying in the axis of a brass tube containing a multiplicity of diaphragms with 1-mm. apertures to define the angle through which the thermopile surface could "see" the flame, the farthest aperture being 71.4 mm. from the thermopile surface. Figure 8 is a diagrammatic plan of the thermopile and flames in two positions, indicating the extent to which the finite size of the apertures permits the thermopile to see flame of a thickness other than that corresponding to full diameter.

The thermopile was calibrated by replacing the flames by an electrically heated sheet-iron plate used as a radiation standard in other work (14). The plate was coated with the Hoffmann-Rubens lampblack-waterglass mixture, which has a high emissivity of about 0.96 (10, 17, 18). The temperature of the plate surface was measured with a platinum-platinum-

rhodium couple of 0.002 inch (0.005 cm.) diameter, peened into a scratch in the surface of the plate. The calibration of the thermopile against this plate yielded a thermopile-galvanometer constant of 1160 B. t. u. of radiation in all directions per square foot per hour, for each millimeter of galvanometer deflection, over a range of radiation of 1500 to 16000 B. t. u./sq. ft./hr. The average deviation of the ten individual calibration points from the average of 1160 was 1.9 per cent.

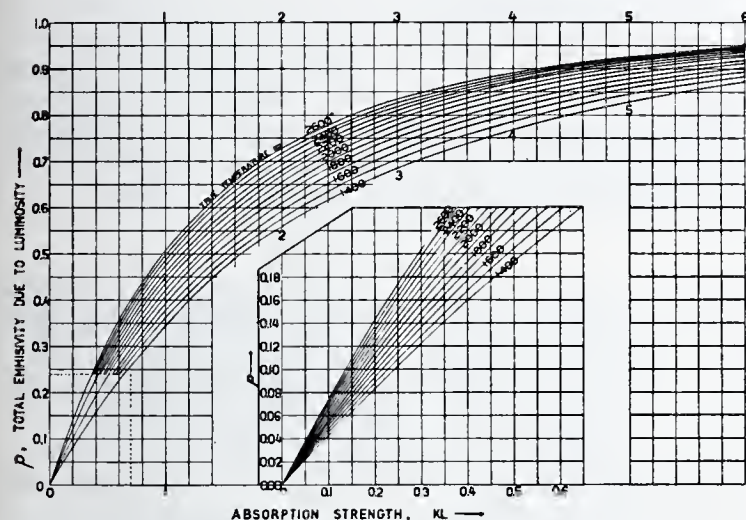


FIGURE 7. PLOT FOR DETERMINING TOTAL EMISSIVITY OF LUMINOUS FLAME FROM ITS TRUE TEMPERATURE AND ABSORPTION STRENGTH

To determine the possible effects of atmospheric absorption of radiation between the flames and the thermopile surface, and of increasing the departure of the system from the ideal condition in which only the center of the flames is seen by the thermopile, measurements were made with the thermopile in two positions, A and B of Figure 8. The average results, given in Table V, indicate that whenever the third flame (farthest from the thermopile) is present in a combination in the A position, the radiation is less than for the same flame combination in the B position. One may conclude, therefore, that the geometrical limitation on the system is operative when a flame is as far from the thermopile as the third flame when the thermopile is in the A position. There is no evidence of trouble from atmospheric absorption.

The average values obtained from the total radiation measurements of Table V are given in Table IV, column c, for comparison with the calculated results. The agreement with theory is quite good, considering that the calculated values depend on an extrapolation of the law of variation of absorption with wave length, that it is impossible to make exact

allowance for nonluminous gas radiation, that the temperature scales of the optical pyrometer and of the rare-metal couple used on the iron plate for calibrating the thermopile are not interrelated by any calibration of one against the other, and that the data on the Hefner flames taken with the optical pyrometer and with the thermopile were obtained by different experimenters and with a time interval of 8 months.

TABLE V. AVERAGE OF MEASUREMENTS WITH THERMOPILE IN TWO POSITIONS

LAMP No.	NO. OF OBSERVATIONS	POSITION	AV. RADIATION	BEST VALUES ^a
1	4	A	8200	
	3	B	8180	
2	4	A	8250	8220
	2	B	8230	
3	3	A	8100	
	2	B	8230	
1 + 2	4	A	15780	
	2	B	15700	
1 + 3	3	A	15360	15560
	2	B	15600	
2 + 3	3	A	14960	
	3	B	15160	
1 + 2 + 3	12	A	22150	22270
	4	B	22270	

^a No weight given to readings in A position with lamp No. 3 as part of system.

APPLICATION TO FURNACE DESIGN

There may be some question as to the exact basis of definition of the quantity, total emissivity of the flame, as obtained from the plot in Figure 8. It is the intensity of total radiation from the flame incident on the surface and normal to it, divided by the intensity of black-body radiation under the same conditions, the black body of course being at flame temperature. A more useful definition would be obtained if the denominator were not black-body intensity normal to the surface, but total radiation in all directions from the surface. The corresponding numerator would then be the radiation in all directions from a flame onto its bounding surface, with the length of the path of the radiant beam constant—i. e., independent of the angle of incidence of the beam. Such conditions are met by only one geometrical figure, a mass of flame of hemispherical shape, radiating to a small element of surface at the center of its base. Only a surface element so placed will "see" the same thickness of flame in all directions. In the case of any actual flame or radiating mass, the length of the radiant beam to a spot on the enveloping surface varies in a complex manner with the angle of incidence of the beam.

This same problem has arisen in connection with the evaluation of radiation from nonluminous gases (11) and powdered-coal flames (8), where it has been shown that it is possible to determine the average length of the path of the beam—i. e., to

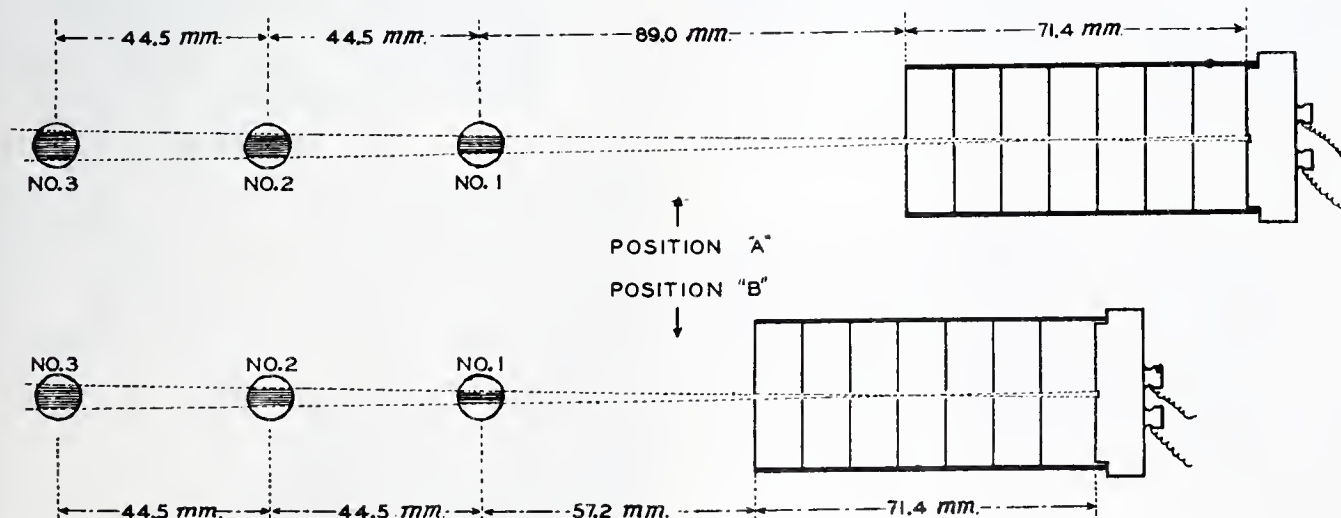


FIGURE 8. DIAGRAM OF THERMOPILE AND FLAMES

substitute for the actual shape of the radiating mass an equivalent hemisphere whose radius bears a definite relation to a characteristic dimension of the shape in question. For example, it is shown that a radiating mass of spherical shape radiates to each unit of bounding surface the same as the standard hemisphere having a radius equal to two-thirds the diameter of the sphere. This equivalent radius of the standard hemisphere might better be called the average distance through which the radiating beam passes to reach the surface, but the term "effective thickness of gas layer" (in this case, flame layer) has been used in the references cited, and will be used here to be consistent. Table VI presents the effective thickness of radiating layer for various shapes.

TABLE VI. EFFECTIVE THICKNESS OF RADIATING LAYER FOR VARIOUS SHAPES

SHAPE OF RADIATING MASS	EFFECTIVE THICKNESS, OR EQUIV. RADIUS OF HEMISPHERE
Sphere	$0.66 \times \text{diam. of sphere}$
Infinite cylinder	$1 \times \text{diam. of cylinder}$
Space between infinite parallel planes	$1.8 \times \text{normal distance between planes}$
Rectangular parallelepiped, $1 \times 2 \times 8$, radiating to a large face	$1.3 \times \text{smallest side}$

The use of Figures 6 and 7 and the above table is perhaps best illustrated by an example. Suppose a furnace is operating with a luminous flame 10 feet long and 4 feet in diameter, circular in cross sections normal to its greatest dimension, and having an estimated area of its envelope of 130 square feet. The two-screen pyrometer, sighted through the flame at points where it is substantially 4 feet thick, gives average readings with the green and red screens of 2034° and 1994° K., respectively, let us say. The total radiation from the flame is sought. From Figure 6, when $T_R = 1994$ and $\Delta = T_G - T_R = 40^\circ$ K., the true temperature T equals 2100° K. and the absorption strength kL equals 0.495. If the flame were an infinite cylinder, the equivalent radius of the standard hemisphere would be directly the diameter of the cylinder, according to Table VI. If the flame were a sphere, the equivalent radius would be two-thirds the diameter. The present shape is between these, and may be estimated as having an equivalent thickness of 0.8 times the diameter of the flame. The average value of kL for the flame then equals 0.8 times the value obtained by sighting through the diameter, or $0.8 \times 0.495 = 0.376$. From Figure 7, when $T = 2100^\circ$ K. ($= 3780^\circ$ R. $= 3320^\circ$ F.) and $kL = 0.376$, the total emissivity p equals 0.21. Then the total radiation from the flame equals $p \cdot A \cdot \sigma \cdot T^4 = 0.21 \times 130 \times 0.172 \times 10^{-8} \times (2100 \times 1.8)^4 = 9,600,000$ B. t. u./hr. If the flame is inside a chamber whose walls have an emissivity of 0.9 and a temperature of 2000° K. ($= 3600^\circ$ R. $= 3140^\circ$ F.), the net heat given up by the flame is approximately (because the emissivity factor is not quite as simple as the product of the emissivity of the flame and that of its surroundings)

$$q = p_F \cdot p_W \cdot A \cdot \sigma (T_F^4 - T_W^4) \quad (13)$$

$$= 0.21 \times 0.95 \times 130 \times 0.172 \times 10^{-8} (2100^4 - 2000^4) 1.8^4$$

$$= 1,620,000 \text{ B. t. u./hr.}$$

Suppose all dimensions of the system were able to be doubled without changing the flame temperature or concentration of soot in it; what would be the increase in flame radiation? The total emissivity would be that value corresponding to $kL = 2 \times 0.376 = 0.752$, or $p = 0.35$. (Note that doubling flame thickness has not doubled flame emissivity.) The flame area will be increased fourfold, and the flame volume eightfold. Per unit of volume of flame, the ratio of the radiation from the large to that from the small flame would be

$$\left(\frac{A_2}{A_1}\right) \left(\frac{p_2}{p_1}\right) \left(\frac{1/V_2}{1/V_1}\right) = \left(\frac{4}{1}\right) \left(\frac{0.35}{0.21}\right) \left(\frac{1}{8}\right) = 0.835$$

The radiation per unit of volume of flame has fallen off, because the outer layers of flame are somewhat opaque to radiation from within. The above illustration is intended to show how data may be obtained on one furnace in actual operation for the purpose of predicting the performance of another furnace of similar shape but different size.

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The authors are indebted to E. R. Smoley, R. D. Hoak, and J. J. Hartz for preliminary thesis work on the problem; to D. M. Gordon and I. M. Dubinsky for some of the experimental work and calculations; to Professor A. C. Hardy of Massachusetts Institute of Technology for the use of his automatic recording spectrophotometer, and to C. H. Gilmour for the measurements of total radiation from the flames.

NOMENCLATURE

- A_λ . Absorptivity, the fraction of a radiant beam of wave length λ , incident on a nonreflecting object, which is absorbed on passage through it.
- c_2 . Constant of Wien equation of energy distribution in the short-wave region of a spectrum of a black body. According to I. C. T., $c_2 = 14330$ micron degrees.
- e . Natural base of logarithms.
- E_λ . Radiation from a black body in the wave-length region λ to $\lambda + d\lambda$.
- k_λ . Absorption coefficient of soot or a luminous flame for radiation of wave length λ . Dimensions = length $^{-1}$.
- k . Constant in equation of variation of k_λ with λ (Equation 3). Multiplied by L , it is called the absorption strength of a flame.
- K . Degrees Kelvin, $= ^\circ \text{C.} + 273$.
- L . Thickness of flame in feet.
- n . Number of flames in a row.
- $p_{\lambda, G, R}$. Emissivity of flame at wave length λ , or λ_G , or λ_R .
- p . Total emissivity, all wave lengths included.
- p_F, W . Total emissivity of flame and surrounding walls, respectively.
- R . Reflectivity, the fraction of a radiant beam incident on a surface, which is reflected.
- S . Apparent low-range or black-body brightness temperature, when an absorbing screen is in the pyrometer.
- Tr . Transmissivity, the fraction of a radiant beam incident on an object, which passes through unabsorbed.
- $T_{R, G}$. Red (or green) brightness temperature, the temperature of a black body having the same intensity of radiation at the wave length λ_R (or λ_G) as the object. In $^\circ$ Kelvin.
- $T_{F, W}$. Flame and surrounding-wall temperature, respectively, in Equation 13.
- α . A constant, an exponent in Equation 3 relating k_λ and λ .
- λ . Wave length in microns.
- $\lambda_{R, G}$. Mean effective wave length of the red and green screens in the pyrometer, respectively.
- λ_m . Effective wave length of color screen in pyrometer, center of gravity of curve of λ vs. product of transmissivity, visibility, and intensity of source.
- λ_m' . Mean effective wave length of color screen in microns.
- μ . Microns (0.001 mm.).
- σ . Stefan-Boltzmann constant $= 0.172 \times 10^{-8}$ B. t. u./sq. ft. and $^\circ$ Rankine 4 and hr.

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Continuous Measurement of pH with Quinhydrone Electrodes—II

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THE quinhydrone electrode has proved itself to be an excellent means for obtaining continuous pH measurements or pH control in many industrial installations. For this purpose it must be installed in a special apparatus which embodies several features essential for the successful application of the electrode.

It is the purpose of this paper to describe briefly a few typical installations of this improved quinhydrone apparatus, to discuss factors essential for its successful installation, to outline the operation of the apparatus, and to give particular attention to the design of the important parts of the apparatus. Various factors such as accuracy, pH range of electrode, limitations of the apparatus, and the time lag of the apparatus in following changes in pH will be discussed.

FIELD OF APPLICATION

For continuous, industrial pH measurements the quinhydrone electrode is being successfully employed in the range of 0 to 8.0 or sometimes 9.0 pH. The electrode may be applied to any solution within this range provided oxidizing or reducing agents which cause a too serious error in the quinhydrone potential are absent. Whether the electrode can be applied in the range from 8.0 to 9.0 pH depends upon the accuracy desired. In most dilute industrial solutions the improved quinhydrone electrode used for continuous pH measurements is accurate within ± 0.05 up to 7.5 pH. Above this pH value the error usually increases gradually, becoming ± 0.1 at 8.0 pH, and approximately ± 0.2 at 9.0 pH. An individual quinhydrone pH measurement, of course, can be made with much greater accuracy in the range 0 to 7.5 pH. However, for most industrial processes the continuous quinhydrone electrode has more than sufficient accuracy.

The improved quinhydrone electrode apparatus, pictured in Figure 1, is limited to solutions to which the quinhydrone electrode itself is applicable and to solutions which will pass freely through the apparatus. Solutions containing suspended materials that retard or stop the flow or those that have considerable foam cannot be measured satisfactorily with this apparatus. In many cases suspended matter may be filtered from the solution easily. For example, in the paper industry the continuous quinhydrone electrode is being applied successfully to white water, but in those cases where the fiber content

An improved apparatus for applying the quinhydrone electrode to continuous pH measurements is described. The error in the reading obtained should not exceed ± 0.05 pH between 0 and 7.5 pH. Above 7.5 pH the error usually increases, becoming about ± 0.1 at 8 pH and about ± 0.2 at 9 pH.

The application of the improved apparatus to several industrial processes and the various essential features contributing to its successful performance are discussed. The time lag of the apparatus, when operating under various conditions, is also discussed and pointed out as being negligible in most industrial applications, but as causing an error of ± 0.2 pH in a few installations.

is sufficiently high to clog the electrode, it has been necessary to filter the test sample. Such liquids may be filtered through a simple screen filter. The white water is allowed to impinge on an inclined screen set at such a pitch that the screen is cleaned continuously, the filtered water being passed through the quinhydrone apparatus.

To avoid red water, the pH of potable water is maintained at the optimum value by liming. A precise adjustment and an economical dosage are obtained by feeding the lime in accordance with the measurements resulting from the use of the special quinhydrone apparatus.

Many boiler-plant operators are employing pH control in the treatment of feed water with alum. For a given water the optimum flock occurs at a definite pH value. It is a well-recognized fact that corrosion in boilers and pipe lines is accentuated by incorrect pH conditions (3).

Some states require industrial waste waters to be above a specified pH value (usually the methyl orange end point) before being dumped into the waterways. The pH of such waste waters (for example, the wash water from a bright dip process (4)) is being controlled and recorded very satisfactorily by the special quinhydrone apparatus.

Other industrial processes in which the quinhydrone electrode may be used profitably for the continuous control or measurement of pH (2) are to be found in textile industries, dye works, color motion-picture film industries, molasses fermentation plants, oil refineries, settling and flotation, and work involving neutralization reactions.

IMPROVED APPARATUS

In a previous paper (1) three important characteristics of the quinhydrone electrode employed for continuous pH measurements were discussed. It was shown (1) that in order to obtain reliable quinhydrone potentials it is essential to maintain, continuously, a quinhydrone concentration of at least 7 mg. per 100 cc. in the flowing test solution; (2) that by giving proper consideration to the solubility of quinhydrone and its rate of solution under various conditions, provision could be made for the continued maintenance of the correct quinhydrone concentrations; and (3) that a platinum electrode is superior to a gold electrode for continuous, quinhydrone, pH measurements.

The improved quinhydrone electrode apparatus includes in its construction and operation not only these important features but also several other unique features in design which



FIGURE 1. IMPROVED QUINHYDRONE ELECTRODE APPARATUS

are discussed below. In general, the apparatus, as diagrammed in Figure 2, is operated as follows:

The solution of which the pH is to be continuously measured is led into the constant head apparatus, *D-1*, by tube *D-2*, and a constant flow of test solution is conducted from the apparatus by the curved rubber tube to the side arm of the flow channel, *F-1*. At this point, a solution of quinhydrone is added, at a constant rate, to the test solution as it passes into the flow channel, *F-1*, flowing downward and then upward through the curved overflow tube, *F-2* and *F-3*. The potential difference between the platinum electrode, *E-8*, and the calomel cell, *E-7*, which are suspended in the flow channel as a single unit, is a direct measure of the pH since the voltage is automatically corrected for temperature variations by a temperature compensator (shown in Figure 1), which is suspended in the flowing solution in the constant head apparatus.

QUINHYDRONE SOLUTION FEED APPARATUS. One of the important parts of the improved quinhydrone apparatus is the unit for introducing a quinhydrone solution into the flowing test solution. The quinhydrone solution which is contained in the reservoir, *A-1*, with a tight stopper, *A-6*, is led into the glass tube *B-4*, in which is situated an alundum filter cup, *B-3*, through pinchcock *A-2*. Immediately below the alundum cup a capillary tube, *B-1*, is cemented into an extended portion of tube *B-4*. The rubber stopper, *A-4*, situated in the top of tube *B-4* bears a tube, *A-3*, which is open to atmospheric pressure, and also the glass tube *A-5*, which conducts the quinhydrone solution from the reservoir to tube *B-4*. The level of quinhydrone solution in *B-4* is fixed by the position of the lower orifice of tube *A-5*. When the quinhydrone solution level falls below the orifice of tube *A-5*, air enters the reservoir displacing some of the quinhydrone solution which flows into *B-4*, reestablishing the former level.

The rate at which the quinhydrone solution passes from the capillary tube into the test solution is governed by the pressure head on the capillary, all other influencing factors being maintained constant. However, in order to allow for slight

variation in capillary sizes and viscosity changes in the quinhydrone solutions, the pressure head may be adjusted by moving tube *A-5* in or out of tube *B-4*, as the case may require. Once made, this adjustment for a particular solution is permanent.

The glass capillary tube has an inverted, flared head to prevent small solid particles from entering the bore of the capillary. The glass tube, *B-2*, which surrounds the capillary tip, not only serves as a protection for it, but also retards the evaporation of the solvent from the quinhydrone solution.

For proper operation of the unit, the flow is adjusted so that about 300 cc. of quinhydrone solution enter the test solution in 24 hours, or approximately 18 drops per minute. Since the solution of quinhydrone contains 30 grams per liter of quinhydrone, and since the test solution is maintained at a flow of 80 to 100 cc. through the flow channel, a simple calculation will show that a concentration of quinhydrone sufficient for a pH measurement exists in the test solution at all times.

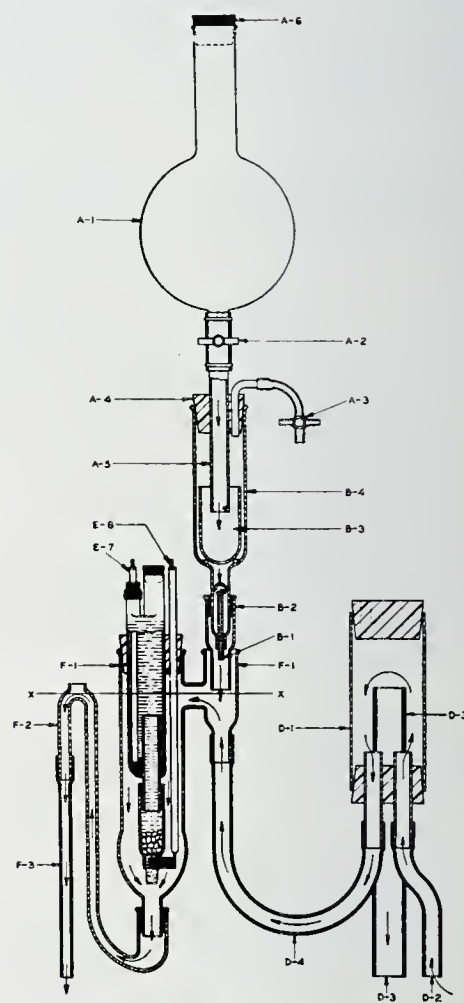


FIGURE 2. DIAGRAM OF IMPROVED QUINHYDRONE ELECTRODE APPARATUS

The solvent for quinhydrone may be acetone, ethyl alcohol and acetone, or methyl alcohol. In any case, the viscosity of the solution is adjusted by the addition of distilled water. In Table I are given the data for various quinhydrone solutions which may be used with the apparatus. The temperature range refers to the temperature of the quinhydrone solution and not to the test solution. If the temperature of the quinhydrone solution falls much below the lower temperature limit, not only will quinhydrone be crystallized from the solution, but the increased viscosity will prevent a sufficient flow of solution through the capillary. A heating unit (for example, an electric lamp) placed close to the quinhydrone unit will maintain the temperature above the lower limit.

TABLE I. QUINHYDRONE SOLUTIONS FOR CONTINUOUS pH MEASUREMENTS

(Quinhydrone concentration, 30 to 31 grams per liter of solvent)

SOLVENT	TEMPERATURE RANGE ° C.
800 cc. of 95% methanol + 200 cc. of distilled water	10-40
900 cc. of 95% methanol + 100 cc. of distilled water	0-20
900 cc. of 95% ethanol + 100 cc. of acetone (government de-natured alcohol No. 23A)	13-40
700 cc. of acetone + 300 cc. of distilled water	10-40
800 cc. of acetone + 200 cc. of distilled water	0-20

THE ELECTRODE UNIT. The saturated calomel electrode and the platinum electrode are held suspended in the flowing test solution by a rubber stopper. The rubber stopper is split vertically on one side, permitting the platinum electrode to be removed easily for occasional cleaning. A semi-circular strip of platinum foil serves as the electrode proper, by which the quinhydrone potentials are measured. The platinum foil is welded to a platinum wire which is sealed into a glass stem. Within the glass stem a copper lead wire is welded to the platinum wire. Sealing wax within the glass stem is fused in intimate contact with the platinum-glass seal. The wax serves a dual purpose in that it first almost entirely eliminates the cracking of the seal, which otherwise occurs frequently, during the cleaning of the electrode, and second, if the seal does crack slightly the sealing wax prevents solutions from coming into contact with the copper wire. In some instances this occurrence has been the cause of serious discrepancies in pH measurements.

The platinum electrode proper is adjusted so as to be situated entirely above the peripheral opening of the ground joint of the salt bridge. This precaution, as well as a downward flow of test solution, prevents excessive concentrations of potassium chloride from coming into contact with the platinum electrode. It was found that in designs which did not observe this precaution, erratic potentials would result from the contact of potassium chloride solution with the metal electrode. Erroneous potentials were especially prevalent in poorly buffered solutions.

The platinum electrode of the calomel cell which dips into the mercury-calomel paste is held in position by a rubber tube, permitting the electrode to be removed easily and to be flexible to shock. The saturated potassium chloride solution in the vessel is maintained at a level higher than that of test solution in the flow channel. Thus, since a one-hole rubber stopper is used in the calomel vessel, there results a slow seepage of the saturated potassium chloride solution through the ground joint. This seepage, together with potassium chloride diffusion from the salt bridge, maintains the liquid junction potential at a small and practically constant value.

TIME LAG

The time lag of the apparatus in following a changing pH is arbitrarily defined as the time required for the pH of the test solution to attain its new value in the neighborhood of the platinum electrode, the time being measured from the instant the test solution with a new pH value enters the side arm of the flow channel. The amount of lag is dependent largely upon three factors: first, the direction in which the pH is changing; second, the magnitude of the pH change; and third, the degree of buffering of the solution.

Considering first the direction of pH change, attention is directed to an extreme example in Figure 3. This curve was copied directly from the recorder paper and was the result of interchanging quickly the flow of city water entering the flow channel with a sulfuric acid solution in city water. The flow in each case was 100 cc. per minute, the volume of water in the flow channel being about 120 cc.

To be more explicit, the quinhydrone apparatus had been operating on city water having a pH of about 6.6 from *a* to *b*

(see Figure 3). At *b* the city water was exchanged for the acid water, the pH dropping rapidly and then more slowly until constant at *c*. At *d* the original water was allowed to enter the flow channel in place of the acid water. The pH increased rapidly and then more slowly until constant at *e*.

It will be noted that the lag in the direction of a decreasing pH is about a fourth of the lag in the direction of an increasing pH. For the explanation of this difference, consider the following example involving two 100 cc. volumes of distilled water, one with a pH of 7.0 and the other previously having

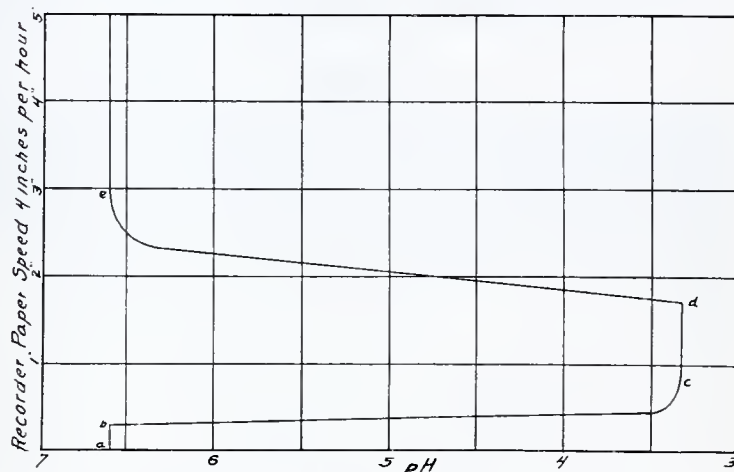


FIGURE 3. ABILITY OF IMPROVED QUINHYDRONE APPARATUS TO FOLLOW CHANGING pH

had its pH lowered to 3.0 by the addition of sulfuric acid. A simple calculation or a pH measurement will show that if 1 cc. of the acidified water is added to the distilled water a large pH change will occur. However, if 1 cc. of distilled water is added to the acidified water, the pH of the solution is practically unchanged.

Essentially the same conditions prevail in the interchange of solutions as described above. The time required for the acidified water to reach the metal electrode is but a few seconds, and with its ability to effect a rapid pH change the lag is small. However, in order that the pH be returned to its former value of 6.6 all of the sulfuric acid must be washed from the flow channel. Hence, the lag in this direction is much larger and is actually a measure of the time required to remove all of the sulfuric acid from the flow channel.

If the difference in pH value of the two solutions is made less the lag becomes correspondingly smaller. Thus, if the lag is measured between two solutions similar to the above except that their pH values are 6.6 and 5.6, the lags are respectively about a third those given in Figure 3.

If a poorly buffered solution flowing through the flow channel is replaced by a strongly buffered solution of a different pH value, the lag is small even though the pH of the buffered solution is higher than that of the unbuffered solution. In reversing the conditions a longer lag, of course, will result. The amount of lag will depend upon the degree of buffering and the magnitude of the pH change.

From this discussion it appears that serious operating difficulties might arise because of the inability of the quinhydrone electrode apparatus to follow a rapidly changing pH. However, such is not the case, because not only are large, rapid pH changes rare in industrial installations, but also it will be noted that even in the extreme example of Figure 3, the major portion of the lag occurs after the pH has changed to a value within 0.2 pH of the correct one. The actual time required in this extreme case for the pH measurement to approach within 0.2 pH of its time value is about 2 minutes for the decreasing pH change and about 10 minutes for the increasing pH. In the most severe industrial test of the quinhydrone apparatus studied to date, the pH as measured

by the quinhydrone apparatus was never more than 0.1 pH different from that of the solution entering the flow channel. Another important fact to be recognized in this connection is that in the majority of industrial installations an endeavor is made to maintain the pH value of a solution within narrow limits. In such cases, the time lag becomes negligible.

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Examination of Electrodeposited Metals and Alloys with X-Rays

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THE methods of x-ray crystal structure analysis may be used for examining electrodeposited metals and alloys to determine their structure, approximate chemical composition, approximate thickness, and relative grain size.

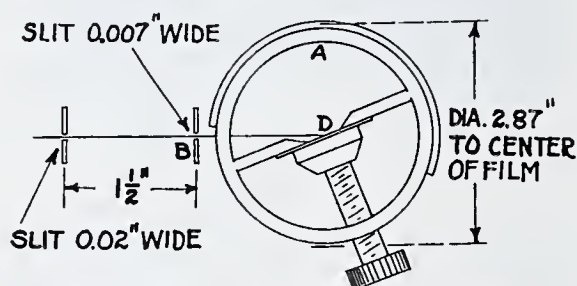


FIGURE 1. X-RAY CAMERA FOR EXAMINING ELECTRODEPOSITED METALS

The theory of the methods has been described in several books on the subject (2, 3, 6, 9, 10) and need not be repeated here. The special apparatus required is illustrated in Figure 1 where the x-rays from a slit at B strike the sample clamped in such a way at D that its surface is on a diameter of the hoop A. The x-rays strike the sample at the center of the hoop and are diffracted so that images of the slit appear on a film held in the opaque paper envelope on the circumference of the hoop. This camera may be modified so that objects of various shapes, instead of flat samples, may be clamped in place. The x-rays may be supplied by a Coolidge tube or by a gas tube. The pictures shown were taken with the radiation from a special gas-type x-ray tube (5) having an iron target, operated at 50 milliamperes and 20,000 volts. At this voltage and current each picture required an exposure of one-half hour. All the photographs shown are full size, but much of the detail observable in the original negatives cannot be seen in the printed pictures. The strong white line which can be seen at the left of each picture was made by the main beam coming from the slit before the sample was clamped in place.

If an object is electroplated with an alloy solely to give it a desired color, as is usually the case, a comparison of colors is the only examination needed to determine whether the deposit is satisfactory. In the cases of alloys which have a constant

color for a wide range of compositions, it is sometimes possible to determine their composition with a sufficient degree of accuracy by means of the methods of crystal structure analysis without stripping the deposit or damaging the electroplated object in any way. With this method it is the crystal structure of the surface layer and not its color of chemical composition which is examined. The relation between structure and chemical composition for many alloys has been investigated. A collection of these results has been published in two volumes by Neuburger (7, 8).

Figure 2 shows photographs of zinc, two kinds of brass, and copper taken with the camera described above. A comparison of these with those given by Westgren and Pragmen (11) indicates that one of the brasses belongs to the alpha phase and the other to the alpha-plus-beta phase. These samples were plated from baths having the following compositions:

ALPHA (1):

Copper cyanide (CuCN), grams.....	27
Zinc cyanide (Zn(CN) ₂), grams.....	9
Sodium cyanide (NaCN), grams.....	54
Sodium carbonate (Na ₂ CO ₃), grams.....	30
Water, liter.....	1
Current density, 0.5 amp./dm. ²	
Temperature, 23° C.	

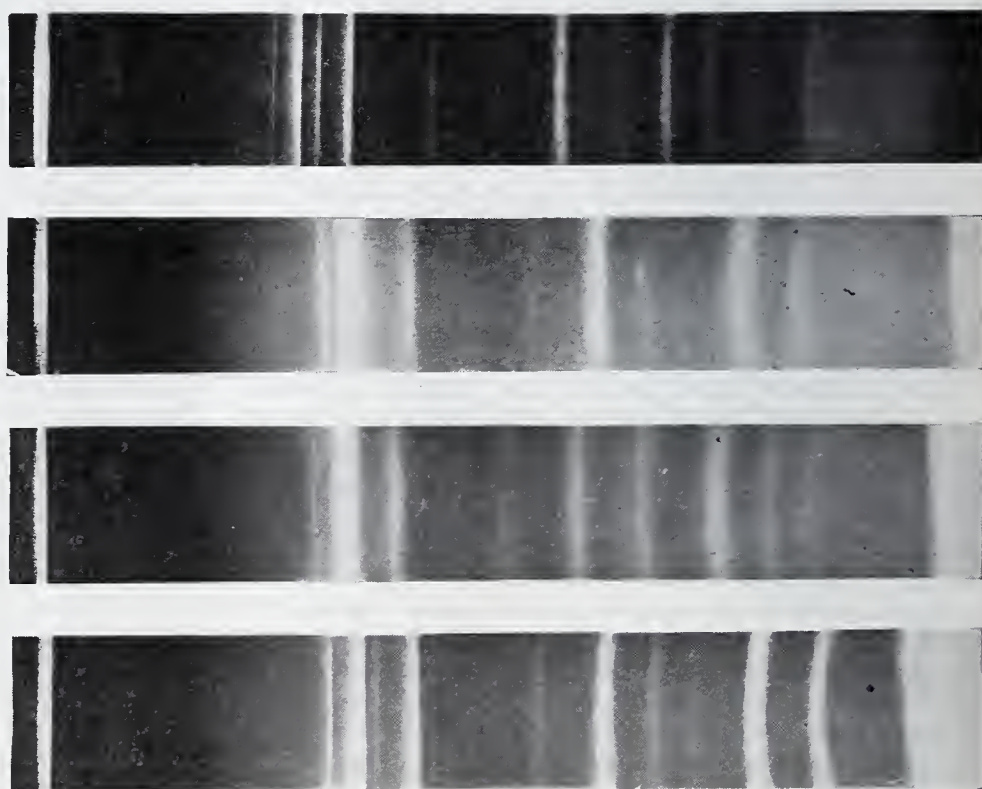


FIGURE 2. ELECTROPLATED BRASS. Top, zinc; upper center, alpha brass; lower center, alpha-plus-beta brass; bottom, copper

ALPHA PLUS BETA:

Copper cyanide (CuCN), grams.....	15
Zinc cyanide (Zn(CN)_2), grams.....	30
Sodium cyanide (NaCN), grams.....	75
Sodium carbonate (Na_2CO_3), grams.....	30
Water, liter.....	1
Current density, 3 amp./dm. ²	
Temperature, 53° C.	

Since the alpha phase of brass may contain from 0 to 36 per cent of zinc, and since the x-ray photographs for this phase do not change appreciably with composition, the x-ray examination does not give very precise information as to composition. The phase containing alpha and beta crystals, however, contains from 36 to 45 per cent zinc, so that the determination of the composition is more exact but much less so than a determination by chemical analysis.

Another illustration of the method is given in the case of copper deposited by "immersion." A piece of tin foil dipped in a solution of copper sulfate is apparently coated with copper in a few seconds. The x-ray photographs show at once that the copper has alloyed with the tin, for (Figure 3) the lines appearing are neither those of tin nor those of copper alone, and are not entirely a super-position of both sets of lines on one photograph.

Cobalt is known to crystallize in both the hexagonal close-packed and the cubic face-centered systems (4). Electrodeposited cobalt usually consists of a mixture of both systems, the relative proportions possibly depending on the conditions under which it is deposited. Figure 4 shows the pictures for two samples of electrodeposited cobalt, one of which is plated from a saturated solution of cobalt formate and the other from a solution of the same composition except that the acidity was changed by adding a small amount of ammonium hydroxide. The temperature and current density in each case were 23° C. and 0.5 amp./dm.², respectively. Possibly because of the two crystal systems present, or for reasons unknown, cobalt does not give good diffraction lines, so that the photographs are not so sharp as others.



FIGURE 3. TIN AND COPPER. Top, tin; middle, tin-copper alloy formed by immersion; bottom, copper

The radiation from x-ray tubes having targets of high atomic number penetrates the material which it strikes more deeply than that from tubes having targets of low atomic number. With a given target, the depth to which the radiation pene-



FIGURE 4. COBALT. Top, from saturated cobalt formate; bottom, less acid solution

trates depends on the voltage at which the tube is operated and on the atomic numbers of the elements through which it passes. This fact makes it possible to use the methods of crystal structure analysis for the relative determination of the

thickness of electrodeposited metals, when the base metal has a structure sufficiently different from that electrodeposited to permit two sets of lines being distinguished on the films.

Figure 5 shows how this method may be applied. The upper picture is of silicon steel. The middle picture was taken of the same sample after it had been given a "flash" of cadmium too thin to be measured with the ordinary micrometer. The strong speckled line of iron at A still shows through the cadmium. The lower picture is the same sample after having been plated with a coating of cadmium 0.015 mm. thick. The speckled line of iron is nearly absent. When determining thicknesses by this method it is necessary to operate the x-ray tube at the same voltage and the same length of time, using the same kind of x-ray films in order to get comparable results. If these conditions are

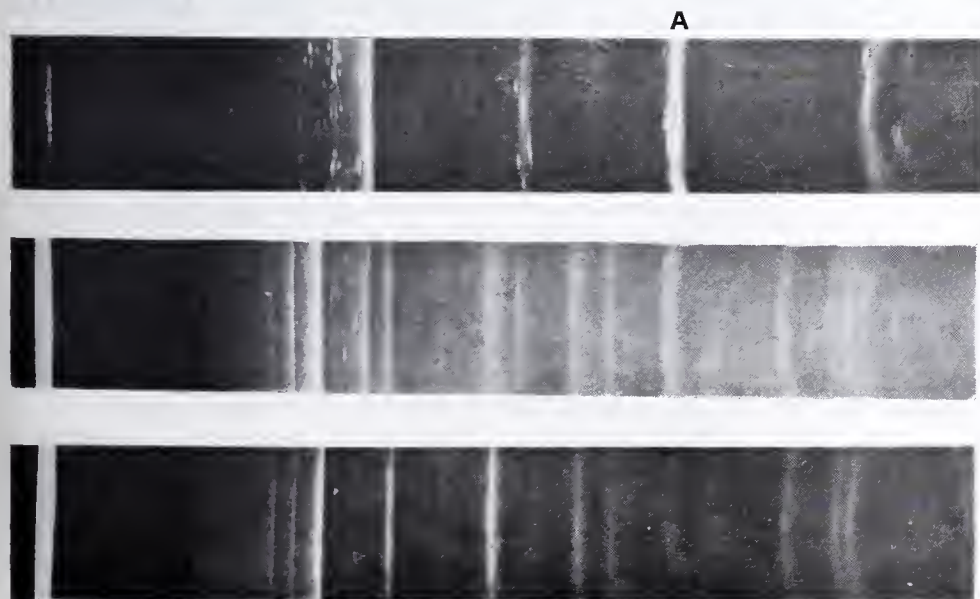


FIGURE 5. SILICON STEEL. Top, silicon steel; middle, with flash of cadmium; bottom, with 0.015 mm. of cadmium



FIGURE 6. COPPER. Top, coarse-grained; bottom, fine-grained



FIGURE 7. BRASS. Top, next to cathode; bottom, away from cathode

fixed, then a photograph of a sample plated with a coating of unknown thickness may be compared with a set of those carefully prepared from samples of known thickness to determine whether the deposit is thicker than required or not so thick. The photographs in Figure 5 also indicate that the x-ray examination concerns itself only with the surface layer when the soft radiation from a target of low atomic number is used.

The relative grain size of electrodeposited metals may also be determined with the same camera. Figure 6 illustrates this for the case of copper electrodeposited from an ordinary acid copper sulfate bath. The top picture shows the speckled

lines given by the coarse-grained copper plated at 90° C., and the bottom picture shows the smooth lines of the fine-grained copper plated at 10° C.

Owing probably to the change in composition of an alloy plating bath during deposition, a thick deposit does not necessarily have the same structure throughout. This is illustrated in Figure 7. The sample for this photograph was plated from the alpha bath at 53° C. and 3 amp./dm.² on stainless steel to which it did not adhere well, and could be stripped. It was 0.35 mm. thick. The top part of Figure 7 is a picture of the side of the deposit which was next to the cathode, and the bottom part shows the structure of the part last deposited. The lines in the lower picture show a shift toward the left, a characteristic of the alpha phase as the percentage of copper decreases.

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Determination of Minute Amounts of Boron in Soils

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MINUTE amounts of boron are essential to the normal development of such plants as the tomato, soy bean, tobacco, and others, but, on the other hand, as little as three to four parts per million by weight in the soil may have a decided toxic effect on other plants. Citrus and walnut trees are seriously affected and sometimes killed by very small amounts, hence the importance of a rapid and accurate method for the testing of soils is evident. Further reference to the effect of boron on the growth of plants will be given in a paper on the analysis of the irrigation waters of Southern California.

Three representative types of methods for the determination of boron are Chapin's modified volumetric method (2, 5), the gravimetric method as outlined by Gooch and Jones (3),

and the colorimetric method originated by Bertrand and Agulhon (1). Large samples of soil are necessary for the determination of small amounts of boron by either the volumetric or gravimetric methods, and not being nearly so rapid as the colorimetric method they are not recommended for the determination of minute quantities of boron in soils.

The modification of the colorimetric method presented in this paper permits the determination of amounts of boron well within the limits that have an appreciable effect on plants. Tests with known amounts of boron as boron oxide, ranging from 0.005 to 1.0 mg., gave fairly accurate quantitative results. The method is applicable to the determination of boron in soils, and satisfactory results may be obtained with samples of soil weighing 100 grams or less. The procedure for the

colorimetric determination as modified and recommended by the authors is as follows:

REAGENTS

Hydrochloric acid, sp. gr. 1.162

Phosphoric acid, 85 per cent

Sodium carbonate, 1 normal

Methanol, absolute

Turmeric solution. Add an excess of turmeric powder to 95 per cent alcohol and filter. In place of turmeric powder, curcumin may be used, as recommended by Pope and Ross (4).
Turmeric paper. Soak a good grade of filter paper in the turmeric solution, squeeze out excess by means of a photographer's roller for mounting prints, dry, and cut into uniform strips.

Standard borate solution. Dissolve 0.2739 gram of sodium tetraborate in water to make a liter of solution. One cubic centimeter of solution contains 0.1 mg. of boron oxide.

APPARATUS

Distillation flask of 250 cc. capacity, supported on water bath; flask carrying a one-hole stopper with long-stem funnel of 50 cc. capacity

Water-cooled condenser 40 cm. long

Platinum dish of 60 cc. capacity

Platinum crucible of 25 cc. capacity

Glass vials 30 mm. high and 6 mm. in diameter

Glass vials 60 mm. high and 12 mm. in diameter

PREPARATION OF SAMPLE

Dry the soil in an electric oven at 105° C. for 24 hours, pulverize, and sift to remove foreign material. Extract 100 grams in 100 cc. of boiling water, allow to stand for about 30 minutes until settled, and then filter, catching the filtrate in a silica dish of sufficient capacity. Silty clay that is finely divided requires several hours for settling, but this may be hastened by salting. Add a small amount of sodium carbonate, evaporate the solution to about 25 cc., then transfer to a platinum dish, evaporate to dryness, and ignite the residue to destroy organic matter. Treat the cooled residue with 10 cc. of phosphoric acid and transfer the solution to the distillation flask. Rinse the platinum dish with 20 cc. of methanol in two or three portions, and transfer the portions to the flask. Distill the solution, collecting the distillate in a platinum dish of 60 cc. capacity. Add 4 to 6 drops of normal sodium carbonate solution to the distillate. About 20 minutes are required for the distillation. Add 10 cc. more of alcohol to the flask through a dropping funnel and make a second distillation, continuing it until liquid ceases to come over. With careful work, the sample being free from water, all boron will be found in the distillates. It is advisable to make a third distillation with 10 cc. of alcohol, testing a drop with turmeric paper and hydrochloric acid to be sure that no boron remains in the residue. If present, complete the distillation, adding this to the main solution.

Evaporate the combined distillates on a water bath at a temperature below boiling, carrying the evaporation to 5 cc. Transfer the solution to a 25- or 30-cc. platinum crucible, and carry the evaporation to dryness. The smaller dish is essential because the quantity of solvent subsequently used is not sufficient to remove the residue from a larger dish.

COLORIMETRIC METHOD FOR BORON

To the cool residue add four drops of hydrochloric acid, sp. gr. 1.162, and 0.5 cc. of distilled water. Transfer to a vial 30 mm. high, rinsing several times with water, and dilute to 2 cc. as shown by a mark on the vial. Immerse a piece of turmeric paper (45 by 3 mm.) in the liquid to a depth of 15 mm. and allow it to soak 3 hours at a temperature of 35° C., or 24 hours at room temperature. (The former is preferred as it gives a more clearly defined coloration.) Compare the height in

millimeters of the red color thus produced against a series of standard papers prepared by soaking strips of turmeric paper in solution containing known amounts of boron treated in the same manner.

Note. This procedure is suitable for quantities of boron oxide ranging from 0.1 to 0.005 mg. Amounts ranging from 1.0 to 0.1 mg. can be determined just as successfully by using larger vials and longer strips of turmeric paper.

Several types of soil were used in testing the effectiveness of this method, the results of the experiments being shown in Table I. A detailed study was made first with sandy loam, and this was followed by more limited experimental work using gumbo and adobe. In addition, samples of soil taken from a number of citrus orchards in Southern California were analyzed, with results as given in Table II.

TABLE I. BORON IN SOILS OF DIFFERENT TYPES

TYPE OF SOIL	WT. OF SAMPLE Grams	B ₂ O ₃ ORIGINALLY FOUND Mg.	B ₂ O ₃ ANNED Mg.	TOTAL B ₂ O ₃ FOUND Mg.
Sandy loam	100	0.05	0.0	0.05
	100	0.05	0.0	0.05
	200	0.11	0.0	0.11
	200	0.12	0.0	0.12
	500	0.25	0.0	0.25
	500	0.25	0.0	0.25
	1000	0.52	0.0	0.52
	100	0.05	0.05	0.11
Gumbo	100	0.05	0.10	0.15
	100	0.05	0.02	0.08
	100	0.5	0.0	0.5
	100	0.5	0.0	0.5
	100	0.5	0.5	0.97
	100	0.5	0.2	0.68
	100	0.3	0.0	0.3
	100	0.3	0.0	0.3
Adobe	100	0.3	0.5	0.76
	100	0.3	0.5	0.76
	100	0.3	0.5	0.76

TABLE II. BORON IN SOILS FROM CITRUS ORCHARDS IN SOUTHERN CALIFORNIA

LOCATION	ORCHARD	TYPE OF SOIL	B ₂ O ₃ FOUND PER 100 GRAMS OF SOIL Mg.
Placentia	Valencia orange	Surface loam	0.200
Yolo County	Lemon	Surface loam	0.075
Yolo County	Lemon	Root zone	0.080
Corona	Lemon	Surface loam	0.055
Yolo County	Valencia orange	Surface silty clay loam	0.060
San Fernando	Lemon ^a	Surface loam	0.300
San Fernando	Lemon	Root zone	0.300

^a Showing slight injury from boron.

Different size samples of sandy loam were used in the testing to determine whether or not small quantities of soil could be used for accurate quantitative determinations as effectively as larger samples. The advantage of using the small quantities of soil is readily seen in that the time required for leaching and evaporating the 100-gram samples would be considerably less than that required for a kilogram sample.

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CORRECTION. E. Lieber and R. Rosen, authors of "Determination of Total Sulfur in Gases" [*IND. ENG. CHEM., Anal. Ed.*, 4, 90 (1932)], wish to add the following acknowledgment to their paper:

The authors appreciate the help of J. B. Lewis of this laboratory who has developed the gravimetric sulfur method and made all the analyses in connection with this work.

An Improved Method of Quantitative Spectrographic Analysis

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IN A previous paper (2) from this laboratory, a general method of quantitative spectrographic analysis applicable to the determination of small amounts of minor constituents and impurities was described. The method is one which has stood the test of several years of constant use and is furnishing satisfactory results. The procedure consisted essentially in comparing the arc spectra of the substance to be analyzed with the spectra of standard samples containing known amounts of the constituents to be determined. The experimental precision is such that duplicate determinations ordinarily vary from the mean by less than 10 per cent of the amount being estimated. Thus if 0.1 per cent is the mean of a series of determinations, the maximum deviation from 0.1 will be ± 0.01 per cent.

The method to be described in this paper is an extension of one suggested by Gerlach and Schweitzer (1, 3). Its essential feature is the introduction into the sample solution, in constant known amount, of an element not originally present therein. This added element is used to furnish spectrum lines of constant intensity, which may serve as comparison standards for estimating the percentages of the constituents to be determined.

Gerlach and Schweitzer have used a similar method in which no added element is required, the comparison of line intensities being between lines of the main constituent and of the minor constituent to be determined. Pairs of lines are found in each of which a certain line of the element to be determined is equal in intensity to a neighboring line of the main constituent. A series of such pairs is found showing equality at different concentrations within the range to be expected. The analysis then consists in observing which of these pairs show equality in the spectrum of an unknown sample. Because of the number and positions of the lines to be paired, it is not always possible to find pairs of suitable intensities close enough together on the plate to be used conveniently. Usually it is better to add an element having a more convenient spectrum than that of the main constituent.

The method of this paper is, briefly, as follows: For a given range of concentration of the constituent to be determined, only one pair of lines is used. With the aid of a recording microphotometer, the relation of the intensities of the two lines of the pair is determined for varying concentrations of the constituent to be determined and a fixed concentration of the added element. A calibration curve is thus established by means of which the intensity ratio for unknown samples can be converted to concentration.

The precision of the previously described method (2) is subject to the limitation that the arc between graphite electrodes is not as steady as is desirable, but wanders about

The method described is an extension of one suggested by Gerlach and Schweitzer, in which the amount of the element to be determined is estimated by measuring the intensity of one of its spectrum lines, using as a basis of measurement the intensity of another line in the same spectrum due to another constituent known to be present in constant amount in all samples of the particular material. A microphotometer is used for measuring the line intensities. The method offers additional reliability and a marked saving in time over the method previously described by one of the authors.

the tips of the electrodes in an erratic way. Constant, alert attention is required on the part of the operator to make sure that the light from the arc shall fall directly on the spectrograph slit throughout an exposure—a condition that is vital to the accuracy of the work. Even under the best possible control there are still unavoidable variations in the arc which undoubtedly result in slight variations in the line intensities on the spectrum plates. For this reason there is always a possibility of error when lines

in one spectrum are compared with those in another, even though both may be on the same plate and thus have had the same photographic treatment.

In the improved method, the lines of the element to be determined and the comparison standard lines are taken simultaneously from the same light source. Any variations, therefore, should affect both in the same way so that they are still comparable no matter what variations have occurred in the arc. This improved comparability now justifies the use of the recording microphotometer for measuring line intensities, a use which was not warranted previously when the errors brought about by the causes mentioned were probably greater than those involved in visual estimates of intensity.

The method here described, therefore, gives more reliable results. In addition, there is a marked saving of time on the spectrograph over the previous method. A single spectrum now serves for one determination where at least five were formerly required.

APPARATUS

The spectrograph, arc stand, electrode holders, and condensing lens system are the same as those described in the previous paper (2).

A rotating sector wheel with adjustable aperture, driven by a small electric motor, is mounted between the light source and the slit so as to interrupt the light beam. This permits the reduction of exposures when necessary without decreasing the angular aperture of the illuminating system below that needed to fill the collimator lens, and without shortening the total time of exposure to such an extent that the sample material is incompletely volatilized. A similar result could be accomplished by using a smaller sample, but this introduces additional possibilities of error. Such control of light intensity is needed in those cases where the most suitable lines for quantitative comparisons are too strong, when full exposure is given, to show properly measurable variations in intensity with variations in concentration. This is a condition frequently encountered, when the *raies ultimes* of an element are so much stronger than the other lines in its spectrum that they are too dense for measurement, even at concentrations so low that there are no weaker lines of that element left in the

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spectrum. The only recourse then is to weaken the entire spectrum to the point where these lines are measurable.

High-purity graphite electrodes are prepared as described in the previous paper.

The microphotometer may be of any suitable type, provided it is of sufficient sensitivity to give a throw of the recording galvanometer beam of at least 20 cm. on the recording sheet between the positions corresponding to complete darkness and

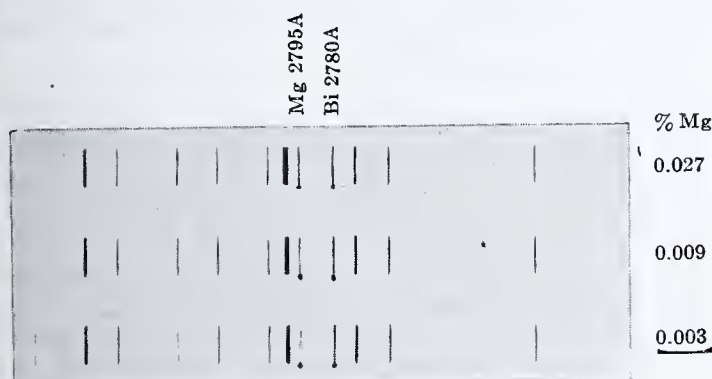


FIGURE 1. STANDARD PLATE SHOWING MAGNESIUM-BISMUTH COMPARISON PAIR

to full illumination through the clear portion of the spectrum background between lines on the spectrum plate. The one in use in this work was constructed in the instrument shop of the Research Division of The New Jersey Zinc Company. It consists essentially of a motor-driven carriage by which the plate can be moved lengthwise across an intense beam of light focused by a lens system into a small area in the plane of the plate. A second lens system focuses an image of the illuminated area of the plate upon a diaphragm immediately in front of a photoelectric cell (a thermopile may also be used). This diaphragm has a slit somewhat shorter and narrower than the images of the spectrum lines focused on it, and parallel to them. This slit serves to admit light to the sensitive surface of the cell, the amount of that light being governed by the density of the portion of the plate whose image covers the slit. As the plate moves, this density varies and a record of the variations is made by a beam of light reflected from the mirror of a galvanometer in the photoelectric circuit, and falling on a sheet of bromide paper moving vertically behind a narrow horizontal slit along which the spot of light from the galvanometer mirror moves.

It is also possible to use a visual or nonrecording type of microphotometer when the procedure would, of course, be modified accordingly.

PROCEDURE

The details of the method can best be described by taking a particular analysis as an example. The application of the method to other analyses can readily be made with only such minor changes in details as may be required by the chemical and physical characteristics of the materials involved.

The analysis to be described is the determination of magnesium in a zinc-base alloy. The magnesium is present in the amount of approximately 0.01 per cent. The added element to furnish the standard comparison spectrum is bismuth. The magnesium line 2795A and the bismuth line 2780A are the two lines forming the comparison pair. These two lines satisfy the requirements for satisfactory comparison lines which may be listed as follows:

1. Under the conditions of the excitation and photography of the spectra, the composition and amount of the sample, and the photometry of the spectral intensities, the comparison lines must be sufficiently intense to make the height of the photometric record for each line great enough so that the photometric peak is clearly distinguishable from the fluctuations in the base

line of the photometer curve. Furthermore, the lines must both be of an intensity which falls within the nearly straight-line portion of the exposure-density curve of the photographic emulsion used.

2. Each line must be separate and distinct from all other lines possibly present in the spectrum. The lines of the comparison pair should be separated sufficiently from each other and from other lines so that there is no possibility of halation effects modifying the relative intensities.

3. The lines should be in that portion of the spectrum where the continuous or background spectrum is very weak.

4. The lines should be close to each other for convenience in photometry and to ensure equal sensitivity of the photographic plate for the two wave lengths.

PREPARATION OF SAMPLE. A known weight of the sample is dissolved in nitric acid and the volume adjusted so that the solution contains 0.25 gram per cc. Two cubic centimeters of this solution are taken and mixed with 2 cc. of a 10 per cent bismuth nitrate solution.

With a capillary pipet exactly 0.1 cc. of this mixed solution is introduced into a hole in one of the drilled graphite electrodes. The electrode is placed in an oven and dried for 45 minutes at 110° C.

EXCITATION AND PHOTOGRAPHY OF SPECTRUM. The procedure for mounting the electrodes, maintaining and focusing the arc, and timing the exposure is the same as that described in the earlier paper.



FIGURE 2. PHOTOMETRIC RECORD OF STANDARD PLATE OF FIGURE 1 (REDUCED)

Using a 3-minute exposure, which is the minimum time allowable for the sample to be completely volatilized, the rotating sector wheel is set for a 10 per cent opening. Under these conditions the selected magnesium and bismuth lines are of suitable intensity for photometry. The extent of the sector opening must, of course, be selected with proper regard to the size, type, and light-transmitting power of the spectro-



FIGURE 3. FIVE SUCCESSIVE RECORDS OF SAME PAIR OF LINES

graph, the speed of the photographic plates, and the intensities of the spectrum lines to be compared.

PHOTOMETRY OF COMPARISON PAIR. After the spectrum plate has been processed in the dark room and dried, it is ready for the photometering operation. The portion of each spectrum which contains the magnesium line, 2795A, and the bismuth line, 2780A, is marked so as to be readily observed without the aid of a magnifier. Figure 1 is a reproduction of a portion of a spectrum plate showing the spectra of three standard solutions corresponding to 0.027, 0.009, and 0.003 per cent magnesium. The bismuth line, 2780A, has equal intensities on the three spectra, since the bismuth is present in equal amounts in the three standard solutions. The magnesium line, 2795A, shows a gradation in intensity.

The plate is mounted on the carriage of the microphotometer and the marked portion of one spectrum is brought into the illuminated field and adjusted so that the lines are vertical and parallel with the slit aperture before the photoelectric cell. They must, of course, be sharply focused on this slit diaphragm. With the aperture covered so that no light can reach the receiving surface, but with all electrical connections closed, the galvanometer mirror is adjusted to bring the recording light beam to a marked zero position on the front of the holder which is to carry the bromide paper. The plate is then moved until the image of the bismuth line, 2780A, is nearly up to the photoelectric-cell slit. The motor drive is started and the line image permitted to cross the slit while the throw of the light beam from the galvanometer mirror is closely observed, and an iris diaphragm on the plate-illuminating lamp is adjusted so that the maximum throw of the galvanometer beam for the 2780 line brings it to a marked point exactly 80 mm. from the zero (dark) position. This may require several trials. (This distance of 80 mm. from the zero applies to the instrument now in use in this laboratory and to this particular determination. It may be varied as required for other instruments and other analyses. The essential point is to set the adjustment so that the peak in the record

corresponding to the standard reference line shall have a definite and constant height.) In this way a compensation is brought about for slight variations in conditions of exposure. An important point to be noted is that measurements are purely relative, requiring constancy in the photoelectric cell and its circuit for only the few seconds during which a single record is being made.

The plate is now returned to the starting position, just short of the first of the two lines to be compared, the bromide paper is placed in the holder, the motor started, and the marked portion of the plate recorded.

As soon as the second of the two spectrum lines has been passed the motor is stopped and the second spectrum on the plate is brought into position in the light beam. Adjustments are made as before and the record taken in the same way on an adjacent portion of the same sheet of bromide paper. All spectra on one plate are recorded on a single sheet.

The paper is then developed, fixed, washed, and dried. Figure 2 shows a photometric record of the magnesium-bismuth pair in the three standard spectra of Figure 1.

EVALUATION OF PHOTOMETRIC RECORD

The evaluation of a record is made by measuring the difference in height of the two peaks in the microphotometer trace, the one due to the magnesium line, 2795A, the other due to the



FIGURE 4. PHOTOMETRIC RECORD OF FOUR SPECTRA FROM SAMPLES OF SAME MATERIAL

bismuth line, 2780A, and correlating this distance with concentration. Table I gives the measurements made on this record.

The definite relation between per cent magnesium and difference in height between the magnesium and the bismuth peaks is determined by measurements of records made from the spectra of solutions prepared for calibrating purposes and

containing known amounts of magnesium. The data from several plates are averaged and used in the preparation of a calibration curve on semi-logarithmic coordinate paper, with linear measurements of differences between peaks on the direct scale and corresponding per cent magnesium on the logarithmic scale. This yields very nearly a straight-line graph which may then be used for interpolation in evaluating the results on analytical samples.

TABLE I. MEASUREMENTS OF RECORD OF MAGNESIUM-BISMUTH COMPARISON PAIR

RECORD NO.	MAGNESIUM %	DIFF. BETWEEN PEAKS Mm.
1	0.027	4
2	0.009	44
3	0.003	84

ACCURACY OF METHOD

The recording microphotometer has been carefully constructed and the technic of using it perfected so that the error to be expected from this step of the procedure is less than the other errors present. Figure 3 shows five successive records of the same pair of lines from the same spectrum. The differences between peaks are given in Table II.

TABLE II. DIFFERENCE BETWEEN PEAKS FROM SAME PAIR OF LINES

(Five successive records)	
RECORD NO.	DIFF. BETWEEN PEAKS Mm.
1	24.7
2	25.0
3	24.3
4	24.0
5	25.0
Av. 24.6 \pm 0.6	

In the routine practice of this method, four electrodes containing the sample to be analyzed are prepared. The four spectra are photographed on the same plate and a photometric record is made of each. The data obtained from a typical case are given in Table III. The photometric record is shown in Figure 4.

TABLE III. DATA OBTAINED FROM FOUR SPECTRA

NO. OF SPECTRUM	DIFFERENCE BETWEEN PEAKS	MAGNESIUM
	Mm.	%
1	41	0.0097
2	38	0.0106
3	41	0.0097
4	39	0.0103
		Av. 0.0101 \pm 0.0005

The maximum deviation of the analyses from the mean is about one part in twenty. In routine practice the error ranges from one part in twenty to one part in ten.

With less expenditure of time greater reliability can be obtained with this method than with the other method described by one of the authors (2). Thus, four check analyses are taken on one plate consisting of four exposures. By the older method four check analyses require four plates of five exposures each.

The chief error in the method seems to be connected with the excitation of the spectra. The arc between graphite electrodes is extremely variable and difficult to maintain centered on the slit. If, during the photography of one of the four check spectra, the arc becomes most erratic while much of the magnesium is being volatilized into the arc, and during the photography of another spectrum the arc remains steady or becomes erratic only after the magnesium is almost entirely expelled from the electrode, the two spectra may not check each other. It is wise, therefore, to take as many as four check spectra in order to give a higher probability of correctness to the average analysis obtained.

ACKNOWLEDGMENT

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Analysis of Nitrous Oxide by Solubility in Water

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METHOD

ALTHOUGH the U. S. Pharmacopeia does not specify at present the percentage purity of nitrous oxide suitable for anesthesia, nitrous oxide is only effective as an anesthetic at concentrations of 90 per cent or higher, and it is therefore desirable at times to ascertain the actual nitrous oxide content of such gas.

As has been shown recently by Bennett (1), the principal impurity, nitrogen, may sometimes be found in concentrations of 10 per cent or more in the gaseous phase of full cylinders of commercial nitrous oxide.

After some consideration of the various physical and chemical methods of determination of nitrous oxide, such as explosion with hydrogen, fractionation at low temperatures, or "washing out" with water, as described by Bennett, a modification of this last method was found to be both accurate and rapid.

The modified apparatus for absorption of nitrous oxide in water is shown in Figure 1. The method differs from that described by Bennett in using water saturated with air, nitrogen, or oxygen in place of air-free water for absorption, and also by introducing a correction factor for the effect of this dissolved gas, instead of a graphical calculation of the percentage of nitrous oxide.

A 10-cc. sample of gas is introduced through stopcocks S_1 and S_2 into the calibrated 10-cc. pipet P , and the pressure and volume adjusted by means of the mercury leveling bulb L . If the pipet is washed out with water before filling with the gas, sufficient water remains on the walls of the pipet and the mercury surface to keep the sample saturated with water vapor. Water saturated with air is then admitted from a flask and siphon, and is allowed to flow through the pipet at

a rate of 10 to 30 cc. per minute. When water is first turned on, the leveling bulb should be lowered slowly so that all mercury may be displaced from the pipet, after which stopcock S_3 is turned so that the water continues to flow through the overflow tube T_1 .

When solution of nitrous oxide is complete, which will be in from 5 to 10 minutes, the volume of undissolved gas is measured after adjusting the water levels in the pipet and overflow tube. The water above the gas bubble is readily expelled through stopcocks S_2 and S_1 to the auxiliary overflow tube T_2 . Further description of the apparatus is prob-

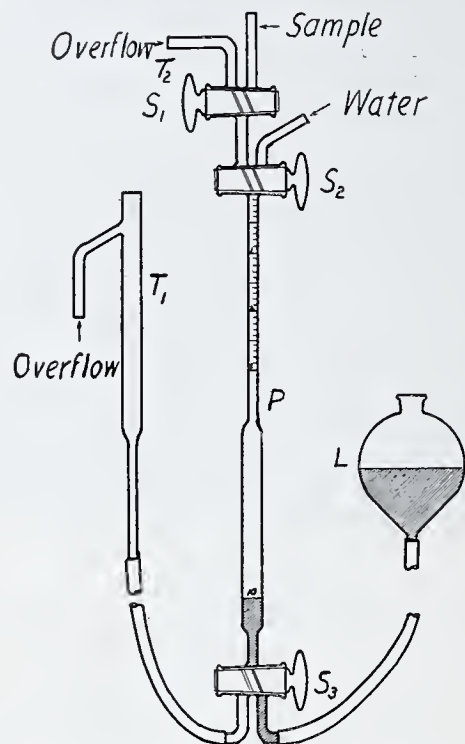


FIGURE 1. MODIFIED APPARATUS FOR ABSORPTION OF NITROUS OXIDE IN WATER

ably unnecessary, except that the pipet was calibrated by weight of mercury, using a water meniscus, however, so as to simulate the conditions under which the final volume is read.

The water is conveniently prepared by immersing an alundum extraction thimble in a flask of water and attaching the thimble to a source of compressed air or other gas. The porosity of the thimble produces many fine bubbles of gas, and saturation is rapidly accomplished.

Care should be taken that the water is at room temperature during saturation and remains at the same temperature without appreciable change during analysis. It is probably more important to avoid supersaturation by a rise in temperature of the water than the reverse.

CORRECTION FACTORS

In order to obtain the true per cent of nitrous oxide in the sample, the per cent of gas dissolved or per cent contraction must then be multiplied by a correction factor. This factor

is to allow for the displacement of air from the water during the process of solution.

The necessity of making a correction of this kind lies in the escape of air from solution, where it is in equilibrium with air at atmospheric pressure, into the gas phase, where the partial pressure of air is zero or small to begin with, increasing to atmospheric pressure at the end of the analysis.

Bennett mentions the displacement of air from ordinary water when used in his method of determination of nitrous oxide, but he did not employ saturation of the water to correct the difficulty.

This factor was first found empirically by using pure nitrous oxide prepared by condensation and fractionation at low temperatures with liquid air. Using this nitrous oxide, the contraction of volume was about 97 per cent when solution was complete at a temperature of 25° C. The correction factor would therefore be 100/97 or 1.031.

The magnitude of this factor suggests a relationship to the relative solubilities of nitrous oxide and air. Factors were then calculated on the assumption that when equilibrium is established, all of the air has been displaced from that volume of water which is just sufficient to dissolve the nitrous oxide. Stated another way, the ratio of solubilities, r , gives the volume of air displaced per cc. of nitrous oxide dissolved and the correction factor is represented by the expression $1/1 - r$.

Table I shows the ratio of solubilities and the calculated factors for obtaining the percentage of nitrous oxide, calculated from data on solubility in the International Critical Tables (2).

TABLE I. SOLUBILITY RATIOS AND CORRECTION FACTORS

TEMP. ° C.	RATIO OF SOLUBILITIES			CORRECTION FACTOR		
	Air:N ₂ O	N ₂ :N ₂ O	O ₂ :N ₂ O	Air	N ₂	O ₂
20	0.0297	0.0254	0.0500	1.031	1.026	1.052
25	0.0313	0.0270	0.0524	1.032	1.028	1.055
30	0.0335	0.0292	0.0558	1.034	1.030	1.059

The data for nitrogen and oxygen are useful in case the water used is saturated with either of these gases instead of air. For the analysis of nitrous oxide-oxygen mixtures, as from an anesthetic machine, the use of oxygen for saturating water is preferable, indeed almost imperative. For the analysis of cylinders of nitrous oxide, the gaseous impurities, consisting largely of nitrogen and a trace of oxygen, are sufficiently close to the composition of the atmosphere to permit the use of air for saturation quite satisfactorily.

RESULTS

The correctness of these calculated factors was tested by analysis of known mixtures of nitrous oxide with air, nitrogen, and oxygen under various conditions of temperature and absorbing liquid. The results of these analyses are presented in Table II. The mixtures were prepared by thoroughly mixing the required amounts of gases in a 100-cc. gas buret, using nitrous oxide which had been carefully fractionated at low temperatures in their preparation.

Table II indicates that results accurate within 0.5 per cent are readily obtained. Duplicate determinations were made for

TABLE II. ANALYSIS OF NITROUS OXIDE MIXTURES

N ₂ O %	A. N ₂ O-AIR MIXTURES			B. N ₂ O-N ₂ MIXTURES			C. N ₂ O-N ₂ MIXTURES			D. N ₂ O-O ₂ MIXTURES		
	Vol. con- traction	N ₂ O by analysis	Error	Vol. con- traction	N ₂ O by analysis	Error	Vol. con- traction	N ₂ O by analysis	Error	Vol. con- traction	N ₂ O by analysis	Error
	%	%	%	%	%	%	%	%	%	%	%	%
100	96.6	99.8	0.2	96.7	99.9	0.1	96.9	99.9	0.1	94.7	99.9	0.1
95	91.6	94.6	0.4	91.3	94.3	0.7	92.1	94.9	0.1	89.8	94.7	0.3
90	86.7	89.6	0.4	86.2	89.1	0.9	87.1	89.7	0.3	84.9	89.6	0.4
85	81.8	84.5	0.5	81.1	83.8	1.2	82.2	84.7	0.3	80.3	84.7	0.3
80	77.0	79.6	0.4	76.2	78.7	1.3	77.3	79.6	0.4	75.5	79.7	0.3
75	72.2	74.6	0.4	70.8	73.1	1.9	72.2	74.4	0.6	70.3	74.2	0.8

CONDITIONS OF ANALYSIS:
A. Water saturated with air; temp., 27° C.; factor, 1.033.
B. Water saturated with air; temp., 26° C.; factor, 1.032.
C. Water saturated with nitrogen; temp., 30° C.; factor, 1.030.
D. Water saturated with oxygen; temp., 24° C.; factor, 1.055.

all mixtures analyzed, and checked each other within 0.1 per cent, which is as close as the volumes may be read.

The total errors in analysis of each mixture are also shown in Table II. The errors involved in preparing the mixtures and also the residual impurities in the nitrous oxide are included in this total error.

It will be noted that the error involved in series B of Table II is much greater than the other determinations. This is to be expected, since the gaseous impurity was pure nitrogen, whereas the water was saturated with air instead of nitrogen. In this case there is a tendency for the more soluble oxygen in the water to be replaced by less soluble nitrogen, with a greater residual volume. Accordingly, for greatest accuracy the water should be saturated with gas having approximately the same composition as the gaseous impurities of nitrous oxide. This makes air a satisfactory gas for saturating the water in the case of commercial nitrous oxide, since the impurities are largely nitrogen and a small amount of oxygen.

The calculated factors of Table I seem to be accurate within the limits of error of the apparatus, since equally good results were obtained on the 100 per cent samples of nitrous oxide, whether air, nitrogen, or oxygen was used for saturating the water.

The apparatus described may be used for determining nitrous oxide by Bennett's method by using air-free water, without any additional modification. It is difficult, however, to determine the absorption rate of a small residual bubble, especially on samples containing more than 98 per cent nitrous oxide. This absorption rate is the essential feature of Bennett's graphical calculation. The use of water saturated with air or nitrogen eliminates this difficulty and considerably shortens the time of analysis.

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Determination of Vanadium in Special Alloy Steels

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IT HAS been shown in an earlier paper (12) that sodium azide is an excellent differential reducing agent for ceric sulfate in the presence of chromic acid. A large excess of azide acting for a considerable time had no reducing action on the chromium. It was pointed out in the same paper that an internal indicator such as diphenylamine or diphenylbenzidine could not be used in the titration of chromic acid with ferrous sulfate if even a small amount of azide were present, as the azide prevented any color development with the indicator. The possibility of removing azide by boiling the solution and of titrating the chromic acid by an indicator method was not studied at that time.

It is obvious that vanadic acid, which is a weaker oxidizing agent than chromic acid, should not be reduced by sodium azide. Therefore, if hydrazoic acid can be removed easily from a solution by boiling, there arises the possibility of determining vanadium in the presence of chromium by oxidizing the former at room temperature with excess of permanganate and removing the excess of oxidizing agent with sodium azide. After boiling off all hydrazoic acid, the vanadic acid could be titrated with standard ferrous sulfate, using diphenylbenzidine as indicator (10). Such a method for vanadium would be of special value in that it would obviate the difficulty experienced by many in determining accurately the end point in the direct titration of a vanadyl salt with permanganate (3) when a considerable amount of chromic salt is present, and also in that it should prove superior in

Vanadium is determined in the presence of chromium by selective oxidation in a cold solution with excess of potassium permanganate, the excess being reduced by sodium azide. All azide is removed by boiling and the vanadic acid titrated with standard ferrous sulfate, diphenylbenzidine being used as internal indicator.

In steels containing tungsten, the tungsten is kept in solution as a complex fluoride, and in this form causes no interference. In such steels diphenylamine sulfonic acid is used as internal indicator in the titration of vanadic acid with ferrous sulfate. This method for vanadium in tungsten steels is more rapid than any of equal accuracy in use at the present time.

A rapid method of oxidizing tungsten in steel to tungstic acid is also described.

speed and simplicity to some of the selective oxidation methods now in use for vanadium, the more important of these being: (1) direct titration of a vanadyl salt with permanganate (3); (2) oxidation with boiling nitric acid (4) to vanadic acid which is titrated with ferrous sulfate electrometrically, a process in which the oxidation is not quite complete; (3) oxidation by permanganate, removal of excess permanganate with hydrogen peroxide in acetic acid solution (8), or by nitrite, followed by urea (6), and titration of vanadic acid with ferrous sulfate electrometrically or with diphenylamine as indicator (2); and (4) oxidation with bromate in a solution containing ammonium salts and a definite

concentration of hydrochloric acid, removal of bromate by boiling, and titration of vanadic acid with ferrous sulfate electrometrically or with an indicator (10). A method has been developed for the determination of vanadium in steels containing not only chromium but tungsten, which is based upon its selective oxidation by permanganate in cold acid solution, and removal of excess permanganate by sodium azide.

The determination of vanadium in steels containing tungsten offers special difficulties. In most methods the tungsten is removed in the form of tungstic acid, this precipitate always carrying with it some vanadium as an impurity. A number of methods have been suggested for the estimation of this small amount of vanadium in the tungstic acid, none of them being entirely satisfactory (10). There is one method for vanadium in which the tungsten is kept in solution throughout the analysis (10), but the end point in the vanadic acid titration in

that case has to be determined electrometrically because tungstic acid prevents any color development with the indicators diphenylamine or diphenylbenzidine.

Since diphenylamine sulfonic acid is an indicator which may be used in the presence of tungstic acid (7), this makes it possible to titrate vanadic acid visually with ferrous sulfate in the presence of tungstic acid. This method offers a procedure for vanadium in steels containing tungsten which is much more rapid than any in use at the present time.

PRELIMINARY EXPERIMENTS

Samples of a dichromate solution containing 0.026 gram of chromium were taken, treated with 5 cc. of sulfuric acid (sp. gr., 1.5), 2 grams of iron as ferric alum, varying amounts of 0.1 *M* sodium azide, 20 cc. of phosphoric acid (sp. gr., 1.37), a little acetate, and water to a volume of 300 cc. To this, 0.6 cc. of a 0.1 per cent solution of diphenylbenzidine was added and 5 minutes allowed for the blue color to develop. With 0.1 cc. of 0.1 *M* azide present, the color development was much more delicate than in the absence of azide, but with 0.25 cc. of the azide in solution it was very difficult to obtain an end point. Therefore, practically all of the azide must be removed before adding the indicator. Experiments with diphenylamine sulfonic acid (7) as indicator showed that a good end point could be obtained in solutions free from azide without buffering, but that the color development of this indicator in the presence of azide was as unsatisfactory as in the case of diphenylbenzidine.

With 5 cc. of 0.2 *M* sodium azide in 300 cc. of a solution containing dichromate, ferric alum, and sulfuric acid boiling for 5 minutes sufficed to remove all hydrazoic acid, and with 10 to 20 cc. of azide present, 10 minutes' boiling was sufficient. Experiments in which the period of boiling was increased to 30 minutes were also satisfactory.

VARYING CONDITIONS IN PERMANGANATE-AZIDE METHOD

Five-gram samples of a chrome-vanadium steel were dissolved in sulfuric acid, the ferrous salt and carbonaceous material oxidized with nitric acid in the usual way, and the liquid boiled for a few minutes to remove oxides of nitrogen. The solution was cooled and diluted with water and phosphoric acid to 300 cc. Potassium permanganate was added slowly with stirring until an excess was present. After allowing the solution to stand for 2 to 5 minutes, the indicated quantity of sodium azide was added and the hydrazoic acid removed by boiling for a definite period. After cooling to room temperature, 30 cc. of phosphoric acid (sp. gr., 1.37), if not already present, enough crystallized sodium acetate to react with the excess sulfuric acid in the solution and 0.6 cc. of 0.1 per cent diphenylbenzidine solution were added. After allowing 5 minutes for the blue color to develop, the solution was titrated with 0.025 *N* ferrous sulfate. Results of a number of experiments are given in Table I.

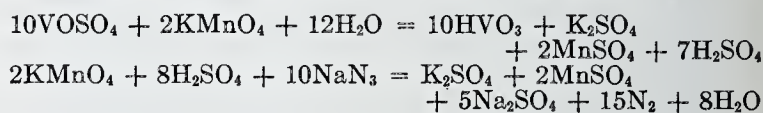
TABLE I. RESULTS OF OXIDATION OF VANADYL SALT

(In presence of chromic salt with excess of permanganate and removal of excess of oxidizing agent with sodium azide)

EXPT.	H ₂ PO ₄ BEFORE OXIDA- TION	KMnO ₄ , 0.025 <i>N</i>	TIME OF STANDING BEFORE ADDING AZIDE	NaN ₃ 0.1 <i>M</i>	PERIOD OF BOILING	VANADIUM
	Cc.	Cc.	Min.	Cc.	Min.	%
1	30	7	2	5	5	0.219
2	30	12	2	5	5	0.221
3	30	7	5	5	5	0.221
4	30	12	5	5	5	0.221
5	0	7	2	5	5	0.219
6	0	12	2	5	5	0.219
7	30	7	2	20	10	0.220

The 7 cc. of permanganate used in four of the experiments represent approximately 0.5 cc. excess. Experiments 2 and 4 show that an excess of 5.5 cc. caused no error. A large excess of azide, as shown in experiment 7, was not harmful. If 10 or

more cc. of azide are added, the solution should be boiled 10 minutes to remove all hydrazoic acid. The azide reacted with the permanganate in a slightly warm solution and all permanganate color disappeared when the solution was below the boiling temperature. The results indicate also that it is immaterial whether the phosphoric acid is added before the permanganate or later. The equations for the oxidation reaction and for the removal of excess permanganate are:



This oxidation method for vanadium was applied to alloy steels. In Table II are given the results of a number of analyses.

TABLE II. VANADIUM IN CHROME-VANADIUM STEELS BY PERMANGANATE-AZIDE METHOD

STEEL	VANADIUM FOUND %
B. S. 30(b) V = 0.215%; Cr = 1.03%	0.215, 0.215, 0.215
B. S. 30(c) V = 0.235%; Cr = 0.977%	0.231, 0.230, 0.231, 0.232
Chrome-vanadium V = 0.212%, peroxide method (8); Cr = 1.00%	0.215, 0.215, 0.211, 0.215
B. S. 73 V = 0.034%; Cr = 13.93% 1-gram samples used and vanadium added 0.516%	0.542, 0.529, 0.526, 0.533
B. S. ferrovanadium 61 V = 31.15%; Cr = 0.52%	31.02, 30.95, 30.97

Five-gram samples of the first three steels were used and 0.2-gram samples of the ferrovanadium. The end points in the last two steels had to be determined electrometrically, the deep green color caused by the large amount of chromium in No. 73 and the deep blue color caused by the large amount of reduced vanadium in No. 61 interfering with the clearness of the color change of the indicator. Table II indicates that accurate determinations of vanadium may be made in steels of widely varying composition. The method is simple and rapid.

STANDARDIZATION OF FERROUS SULFATE

The ferrous sulfate used in the analyses in Table II was standardized electrometrically against standard ceric sulfate (11) whose strength had been determined electrometrically against Bureau of Standards sodium oxalate (11). Since dichromate is the primary standard more commonly used in this standardization and since its oxidizing power toward ferrous sulfate has been shown to vary considerably with dilution (1, 9), it seemed important to determine the correct conditions under which to standardize ferrous sulfate for vanadic acid titrations.

Samples of 50 cc. of 0.1 *N* ammonium vanadate, each with the same acidity, required, when titrated electrometrically in volumes of 100 and 600 cc., 53.59 and 53.58 cc. of a ferrous sulfate solution. In contrast to the titration of chromic acid with ferrous sulfate, the result is not influenced by the volume of the solution. A ferrous sulfate solution standardized electrometrically against standard ceric sulfate was found to be 0.02757 *N*, and when standardized against very pure dichromate by the following procedure was 0.02752 *N*. Because of this good agreement between the two methods, this procedure is recommended: Weigh out samples of 0.05 to 0.06 gram of pure potassium dichromate, dissolve in a little water containing 3 cc. of sulfuric acid (sp. gr., 1.83). Add sufficient ferric sulfate or ferric alum solution, free from ferrous iron, to be equivalent to 0.1 gram of iron, 10 cc. of phosphoric acid (sp. gr., 1.37), and dilute to 300 cc. Add 15 grams of crystallized sodium acetate, and, when dissolved, 0.6 cc. of 0.1 per cent diphenylbenzidine. Allow 5 minutes for the brownish color to develop and titrate with 0.025 *N* ferrous sulfate. An

indicator correction of 0.03 cc. per 0.1 cc. of indicator used should be added to the volume of ferrous sulfate (10).

VANADIUM IN CHROME-VANADIUM STEELS

A sample of 4 or 5 grams is convenient when the per cent of vanadium is low (0.15 to 0.25 per cent). Place it in a 600-cc. beaker, add 30 to 40 cc. of water, and run in a measured volume of sulfuric acid (sp. gr., 1.83) from a buret. Each gram of iron requires 1.5 cc. of concentrated sulfuric acid for final conversion into ferric sulfate. If an excess of 2 to 2.5 cc. of acid is allowed, the process of solution is rapid.

After the steel has been completely decomposed, boil until a considerable quantity of salts separates out, in order to assist in decomposing carbides. Dilute with 20 cc. of water and heat until the salts have dissolved. Add nitric acid (sp. gr., 1.42), drop by drop, to the hot liquid until the violent oxidation of ferrous sulfate is over (3 to 3.5 cc. of acid are sufficient). Boil the solution to destroy oxides of nitrogen, cool to room temperature, add 30 cc. of phosphoric acid (sp. gr., 1.37), and dilute to 300 cc. Add 0.1 *N* potassium permanganate from a buret until an excess is present. Then add three or four drops more and let the solution stand for 2 minutes to be sure that the color persists and all of the vanadium is oxidized. Add 5 cc. of 0.1 *M* sodium azide¹ and boil vigorously (in hood) for 5 minutes to remove all hydrazoic acid. If more than 5 cc. of azide are used the solution must be boiled for 10 minutes. Cool to room temperature and add 15 grams of crystallized sodium acetate. (This should be the correct amount of acetate to react with the 2 to 2.5 cc. excess of sulfuric acid used in dissolving the steel and with the slight amount of nitric acid present. If too much acetate is added so that a permanent precipitate forms, a drop or two of sulfuric acid will cause the solution to clear.)

As soon as the acetate has dissolved, add 0.6 cc. of 0.1 per cent diphenylbenzidine solution, prepared by dissolving 0.1 gram of the reagent in 10 cc. of concentrated sulfuric acid and diluting this with 90 cc. of glacial acetic acid. Allow 5 minutes for the color to develop, and titrate with 0.025 *N* ferrous sulfate. The correction to be applied for the indicator is added to the volume of ferrous sulfate and amounts to 0.03 cc. of 0.025 *N* ferrous sulfate per 0.1 cc. of indicator. The end point is very sharp.

Diphenylamine sulfonic acid (?) may also be used, in which case no acetate is necessary. The titration must be begun as soon as the indicator is added, because the color disappears on standing. The blank is greater with this indicator.

VANADIUM IN STEELS CONTAINING TUNGSTEN

The permanganate-azide method is applicable to such steels. A modification in procedure is necessary, however, to keep the tungsten in solution. Two different procedures have been tested. In one, the tungsten, after oxidation to tungstic acid, is filtered off, dissolved in sodium hydroxide, and poured back into the main solution to which hydrofluoric acid has been added. The tungstic acid forms with the hydrofluoric acid a soluble complex fluoride. In the other, the sulfuric acid solution of the steel containing metallic tungsten in suspension is treated with nitric acid in the presence of hydrofluoric acid. The ferrous iron and nearly all of the tungsten are oxidized in this way, the tungstic acid remaining in solution as a complex fluoride, the tungsten, however, apparently not entirely in the hexivalent form. Persulfate is used to oxidize the remainder of the tungsten. If this is not done, low results for vanadium are invariably obtained. The excess persulfate is removed by boiling and a little ferrous sulfate added finally to reduce any traces of persulfate which might remain. In either procedure, permanganate is then

used in excess to oxidize the vanadium, azide added to destroy the excess of permanganate, and the solution boiled to remove all azide. After cooling the solution to room temperature, sodium diphenylamine sulfonate is added as internal indicator and the vanadic acid titrated with standard ferrous sulfate. It is not necessary to reduce the acidity to obtain a sharp color change at the end point.

Experiments in which phosphoric acid was used in place of hydrofluoric acid to keep the tungstic acid in solution were not successful, as was to be expected from earlier work by the same authors (10) in which it was shown that, in the presence of phosphotungstic acid, vanadic acid forms a complex which is only partially reduced by ferrous sulfate.

A few quantitative results were obtained using hydrochloric acid instead of hydrazoic acid as the reducing agent for the permanganate, but this method was not so satisfactory because of the closer control of conditions required. The presence of silver chloride was necessary (5) to obtain complete reduction.

The amount of hydrofluoric acid (48 per cent) required to keep in solution throughout an analysis the tungstic acid from a 1-gram sample of steel containing 20 per cent of tungsten was found to be 5 cc. Just before the addition of the indicator and the titration with standard ferrous sulfate, 3 cc. more of the hydrofluoric acid were added. Otherwise the change in color of the indicator at the end point was often unsatisfactory. With this additional hydrofluoric acid, the color change was always very sharp. The action of the hydrofluoric acid in the hot solution upon the glass beaker is very evident, but a beaker may be used for a great many determinations before becoming too thin for use.

The indicator correction for diphenylamine sulfonic acid is larger than for diphenylamine or diphenylbenzidine (?). For a given amount of indicator, however, the correction remains constant if the titration is made immediately after the addition of the indicator. The correction can be determined for a supply of indicator solution by determining vanadium in a standard steel, or it can be eliminated by standardizing the ferrous sulfate against sufficient standard dichromate to require about the same volume of solution as used in the determination of vanadium, since Sarver and Kolthoff (?) have shown that the indicator correction for the dichromate-ferrous iron titration is approximately the same as for the vanadic acid-ferrous iron titration. Before titrating the chromic acid, sulfuric acid, hydrofluoric acid, and ferric iron should be added as well as the indicator. The correction may be eliminated by using indicator which has first been oxidized and then reduced by ferrous sulfate (6) as described later, or by electrometric titration.

PREPARATION OF INDICATOR. A 0.005 *M* solution of diphenylamine sodium sulfonate is prepared by dissolving 3.2 grams of the barium salt (?) in a liter of water, adding to this solution a slight excess of sodium sulfate, and decanting the clear liquid. A convenient amount to use in a titration is 0.3 cc. of this solution.

RAPID OXIDATION OF TUNGSTEN

Special attention should be called to a procedure used in Method B (see later part of paper) for the oxidation of tungsten by nitric acid by means of which the time for a tungsten determination in a steel may be greatly shortened. Add 10 cc. of water and 30 cc. of hydrochloric acid (sp. gr., 1.18) to a 1-gram sample of the steel in a 400-cc. beaker. Warm gently until the steel is completely decomposed and the tungsten separates out as a black powder. Make sure by swirling the liquid in the beaker while tilting it that no particles of tungsten stick to the bottom. Add five or six drops of nitric acid to the boiling-hot liquid and mix thoroughly by tilting the beaker and giving the liquid a rotary motion.

¹ Sodium azide and barium salt of diphenylamine sulfonic acid may be obtained from the Eastman Kodak Company, Rochester, N. Y.

Repeat this treatment, with a few drops of nitric acid and steady swirling of the liquid, two or three times, keeping the liquid boiling hot and giving plenty of time between the addition of each portion of nitric acid for all action to be completed. In this way all of the tungsten will usually go into solution just before any tungstic acid separates out. Thus there is no chance for particles of tungsten to become coated with tungstic acid, and the protracted period of boiling with nitric acid, often necessary to oxidize all of the tungsten, is reduced to 5 or 10 minutes. Add the remainder of the nitric acid (use 10 cc. in all) and boil down to 20 cc. From this point the usual procedure for a tungsten determination is followed.

VANADIUM IN CHROME-VANADIUM-TUNGSTEN STEELS

The results obtained for vanadium in a number of chrome-vanadium-tungsten steels are given in Table III. In Method A, the tungsten was oxidized by nitric acid and persulfate in the presence of hydrofluoric acid, and was thus kept in solution throughout the analysis. In Method B, the tungstic acid was filtered off, dissolved in sodium hydroxide, and returned to the main solution to which fluoride had been added.

TABLE III. VANADIUM IN CHROME-VANADIUM-TUNGSTEN STEELS

STEEL	VANADIUM FOUND					
	Method A			Method B		
	%			%		
B. S. 50	0.758, 0.753			0.746, 0.763		
V = 0.756%; Cr = 3.61%; W = 17.56%	0.766, 0.756			0.744, 0.748		
B. S. 50(a)	0.975, 0.982			0.921, 0.940, 0.962		
V = 0.976%; Cr = 3.52%; W = 18.25%	0.982, 0.974 0.974, 0.983					
No. 1	1.32, 1.32, 1.32	1.28, 1.29, 1.28				
Cr = 3.11%; W = 19.1%						
No. 2	1.90, 1.90, 1.90	1.84, 1.86 1.88, 1.85				
Cr = 4.10%; W = 14.3%						
No. 3	3.56, 3.57, 3.57	3.53, 3.53 3.50, 3.53				
Cr = 4.03%; W = 17.1%						

These results show the close checks obtained in duplicate analyses by Method A. The values from this method are slightly higher always than those from Method B, possibly because of the more complete oxidation of the tungsten in Method A. This method requires less time than Method B and appears more accurate. The indicator blank in these analyses amounted to 0.40 cc. of 0.025 *N* ferrous sulfate for the 0.3 cc. of indicator used. The indicator solution contained approximately 0.3 per cent of the sodium salt.

Experiments using Method B were carried out in which 1 gram of persulfate was added to the filtrate from the tungstic acid after the precipitate had been returned to the solution as a soluble complex fluoride. These solutions were boiled for 5 minutes, then 5 cc. of 0.1 *N* ferrous sulfate were added to the hot solutions to destroy any persulfate which might remain. After cooling, the solutions were treated with excess of permanganate and the usual procedure followed from this point. The results with this modified procedure were the same as those given for Method B in Table III. The cause of the slightly low results from this method were not investigated further, as obviously the more rapid procedure in Method A is preferable. Lang and Kurtz (6) whose paper appeared after this work was completed, obtained satisfactory results by making a separate titration of the vanadium in the tungstic acid, which had been dissolved as in Method B.

METHOD A. Tungstic acid is kept in solution as a complex fluoride throughout the analysis. Add 25 to 30 cc. of water and 4 cc. of sulfuric acid (sp. gr., 1.83) to a 1-gram sample of the steel weighed into a 400-cc. beaker. Warm gently until the steel is completely decomposed and the tungsten separates out as a black powder. Add five or six drops of nitric acid (sp. gr., 1.42) to the boiling-hot solution and, while tilting the beaker, swirl the liquid thoroughly. Then add 5 cc. of

hydrofluoric acid (48 per cent) and more nitric acid, using 5 cc. of nitric acid in all. Boil 2 minutes. A solution of clear greenish color is obtained. Occasionally some tungstic acid will precipitate at this point, but adding the hydrofluoric acid sooner will usually prevent this.

Dilute to approximately 100 cc., add 1 gram of ammonium persulfate, and boil 5 minutes. Add 5 cc. of 0.1 *N* ferrous sulfate, dilute to between 150 and 175 cc., and cool to room temperature. Add to this solution 0.1 *N* potassium permanganate from a buret until a distinct color persists for 2 minutes, to be sure all of the vanadium is oxidized. Add 5 cc. of 0.1 *M* sodium azide and boil vigorously (in hood) for 5 minutes to remove all the hydrazoic acid. Cool to room temperature, add 3 cc. of hydrofluoric acid (48 per cent), 0.3 cc. of a 0.005 *M* solution of diphenylamine sulfonate, and titrate within a minute with 0.025 *N* ferrous sulfate. The color change of the indicator at the end point is from purple to green. The correction to be applied for the indicator must be determined and added to the volume of ferrous sulfate used in the titration.

Lang and Kurtz (6) used diphenylamine in the presence of the complex tungsten fluoride. The color change is, however, not satisfactory when it is substituted in the above method.

Instead of using azide to reduce the excess of permanganate, good results were obtained by adding a slight excess of nitrite and removing the excess by the immediate addition of 5 grams of urea, as directed by Lang and Kurtz (6). The solution was allowed to stand 15 minutes before adding the indicator.

VALUE OF INDICATOR CORRECTION FOR DIPHENYLAMINE SULFONIC ACID

This value may be obtained from duplicate analyses of a standard chrome-vanadium-tungsten steel, preferably a Bureau of Standards steel, using the procedure given above under Method A. If 0.3 cc. of 0.005 *M* diphenylamine sulfonic acid is used for the standard steel, the difference between the theoretical volume of 0.025 *N* ferrous sulfate required for the known quantity of vanadium present and the actual volume used for the vanadic acid will represent the indicator correction to be added to the volumes of 0.025 *N* ferrous sulfate used in analysis of other steels. The ferrous sulfate solution should be standardized against standard dichromate, using the procedure given in the first part of this paper.

To prepare an indicator with no blank correction take 0.3 cc. of the solution, 5 cc. of water, 3 or 4 drops of concentrated sulfuric acid, 3 or 4 drops of 0.1 *N* dichromate, and add very dilute ferrous sulfate until the purple color just turns to a bluish green. The purple color will appear when the first few drops of ferrous sulfate are added. Add this bluish green solution to the solution to be titrated.

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The Turbidimeter in Paint Manufacture

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THE principles of turbidimetry or nephelometry have been used a great many years, and slight modifications in their application have been made to adapt turbidimeters to specific uses. Applying the use of the turbidimeter to the paint and pigment industry has proved very helpful in judging the merits of pigments and paints.

The turbidimeter used in these laboratories and shown in Figure 1 is a modification of the one described by Vogt (3). The fundamental principle of the apparatus is the obscuring of the lamp filament by gradually increasing the height of the column of suspension which is mounted directly over the filament. The turbidimeter consists essentially of a right-arm Kennicott-Sargent colorimeter tube mounted over a single-strand straight-filament galvanometer-type bulb, which is a 3.5- to 4.0-volt bulb in series with a 60-watt 120-volt bulb on a 120-volt circuit. A slit diaphragm is mounted over the bulb to allow only direct light from the filament to pass up through the suspension, whereby most extraneous diffuse light is eliminated. The plunger held by a friction clamp is used to force the suspension from the long arm to the calibrated arm of the tube and hold it constant while recording readings. The small rectangular box shown in Figure 1 is placed over the calibrated arm to exclude extraneous light when obtaining the end point.

Obscuring power is usually expressed in square centimeters per gram and is calculated as follows:

Let W = weight of pigment in grams
 V = total volume of suspension in cc.
 H = height of suspension in cc.

$$\text{Obscuring power} = \frac{V}{WH} = \text{square centimeters per gram}$$

This figure multiplied by the specific gravity of the pigment gives the obscuring power on the volume basis—that is, square centimeters per cc.

The following precautions should be adhered to when making observations:

Vehicles being used for the suspensions should always be filtered.

The end point should always be obtained by raising the level of the suspension until the filament just disappears, and not by lowering the level of the suspension until the filament reappears. The point of disappearance is sharp and does not require prolonged observation. Three or four readings should be taken from each suspension, the average being used as the end point.

Large variations in room temperature should be avoided or corrected for when comparative results are desired.

It is well to regulate the concentration so as to have the end point between 2.5 and 4.0 cm. However, concentrations may be varied 100 per cent with practically no change in derived obscuring power.

It is a well-established fact that the properties such as tinting strength and hiding power of pigments vary materially with changes in particle size. The measurement of the turbidity of a suspension has proved itself to be an excellent,

The turbidimeter is being used to estimate the relative fineness of pigments and powders, to determine the relative degree of incorporation or dispersion of a pigment in a vehicle, to determine the relative obscuring power of one white pigment to another, and to judge the merits of grinding mills. A relation has been established between obscuring power and hiding power and between obscuring power and tinting strength, whereby the turbidimeter test is used to give both the hiding power in square feet per pound and tinting strength on the basis of white lead as 100. The turbidimeter is also used to determine if the pigment or powder consists mostly of colloidal particles.

rapid means of measuring the average relative fineness of samples of a single pigment—that is, one sample of white lead against another sample of white lead, or one sample of titanium oxide against another sample of titanium oxide. One pigment cannot be compared directly against another for relative fineness by this test. The turbidimeter can be calibrated into units of fineness by microscopical sizings of a number of samples sufficient to cover the fineness range. Then the obscuring power can be read in terms of fineness, if the calibration has been made properly.

Suspensions for the determination of relative fineness of fine pigments such as white lead are usually made up of water or light-bodied linseed oil. First 0.125 gram of white lead, 0.05 gram of gum arabic, and 0.05 gram of saponin are accurately weighed out, then transferred to an agate mortar, and two drops of distilled water added. The mixture is rubbed up until a semi-dry tacky paste is formed, when one more drop of water is added. Incorporation should be kept up for about 10 minutes, adding more water if necessary to keep the paste tacky. The paste is diluted to 200 cc. in a volumetric flask, shaken thoroughly to a uniform suspension, and poured into the long arm of the turbidimeter tube to eliminate air bubbles in the calibrated arm. Pressure is applied to the plunger and the height of suspension necessary to obliterate the filament noted. The same procedure is followed when using oil, but no additional agents are required.

Pigments which have individual particles large enough to be broken down by the incorporation in the mortar are made up as follows: Of the pigment, 0.2500 to 0.3000 gram is weighed out accurately and transferred to a 600-cc. beaker, one drop (25 mg.) of linseed oil added, and the mixture briskly brushed over the entire bottom of the beaker for at least 10 minutes. If the mixture becomes too dry, another drop of oil should be added. It is important to use a stiff-bristled brush for this test. A small brush, approximating 0.25 inch (0.63 cm.) in diameter, with the bristles cut to about 0.37 inch (0.90 cm.) to increase the stiffness, is a very good size. This

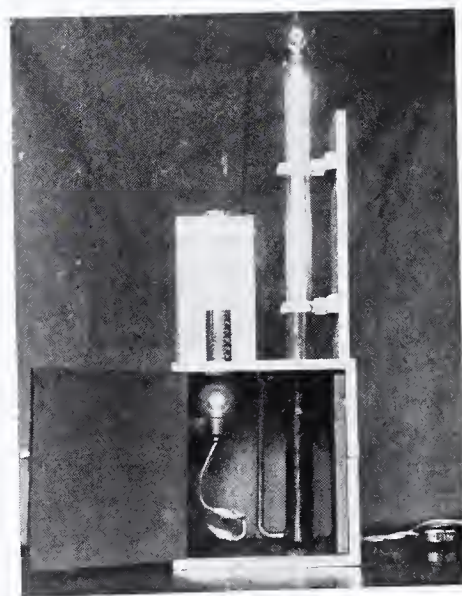


FIGURE 1. THE TURBIDIMETER

treatment breaks down agglomerates without affecting the individual particles. Then 20 cc. of linseed oil are added, the mixture stirred until the suspension is uniform, diluted to 200 cc., stirred to uniformity, and the obscuring power determined. These tests give the ultimate obscuring power of the pigment.

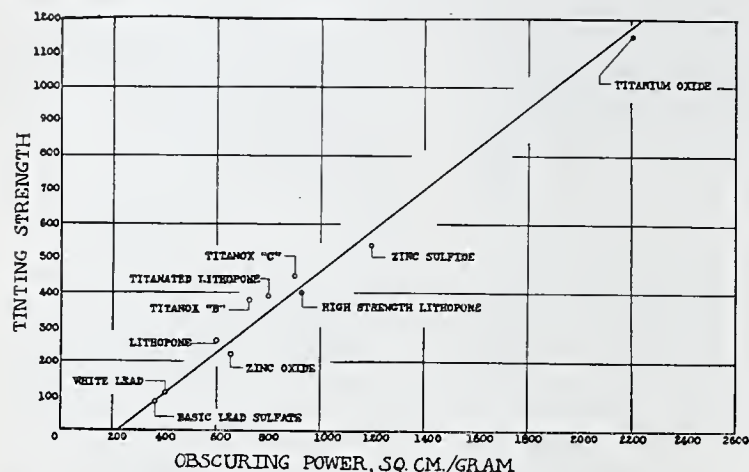


FIGURE 2. RELATION BETWEEN OBSCURING POWER AND TINTING STRENGTH

If the pigment or powder consists of quite coarse particles which are easily broken down, signifying that it is a soft material, a soft pliable-bristled brush should be used for the incorporations. Another means of incorporating the coarser powders is to wash and brush the powder through a 400- or 200-mesh sieve with a good wetting vehicle.

By studying a few suspensions under the microscope the best method of incorporating groups or types of pigments can be determined. Once the approximate average fineness of the powder has been established microscopically, the general fineness of the incorporated suspension can be compared to it. If the suspensions are too coarse, owing to agglomeration, or too fine, owing to grinding by the means of incorporation, they should not be used for test. When the proper degree of incorporation has been attained, the fineness of the suspension will be very similar to the original powder. It is best to use that type of incorporation which allows the most mechanical action on the pigment without changing its state of fineness. The microscope is also used to see if the pigment tends to flocculate quickly after being dispersed.

When a pigment is made into a paste or paint, the particles of pigment are "dispersed"—that is, separated and suspended in the vehicle. Particles may be agglomerates or individual ones. The degree of dispersion may be considered as the extent to which agglomerates are broken down, complete or ultimate dispersion signifying that all particles in the paint are individual ones. The degree of dispersion depends upon several factors, such as character of pigment, the nature of the vehicle, and the methods and care used in making the paste or paint. The degree of dispersion in a paint affects its properties, as, for instance, poor dispersion in a red lead paint tends to cause sagging or running of the paint films. Hence in relation to the fineness of particles in paint, we must consider the "ultimate working units." According to the A. S. T. M. nomenclature, the ultimate working unit may be an individual particle or any group of individual particles that are so firmly held together by forces of adhesion that they remain intact as a group throughout the duration of their application.

To determine the relative degree of dispersion of pigment in a paste or paint accurately, approximately 0.1 gram of paint of fine pigments and approximately 0.3 to 0.4 gram for the coarse pigments are weighed into a 100-cc. beaker. Ten to twenty cubic centimeters of linseed oil are added and mixed thoroughly with a brush like that specified above but with the bristles uncut so that they will be more pliable. The mixture is

poured into a 600-cc. beaker, and all the paint transferred from the 100-cc. beaker to the 600-cc. by repeated washings and brushings with more oil. It is then diluted to 200 cc. with linseed oil, stirred until the suspension is uniform, and the obscuring power determined. Comparing this result with the ultimate obscuring power of the pigment indicates the degree of dispersion in the paste or paint.

For practical purposes, this treatment preserves the relative dispersion in the sample, because agglomerates are not readily broken down by mixing with a pliable-bristled brush in a large proportion of oil. It has been the writer's experience that both good wetting by the vehicle and good mechanical action are necessary to break down agglomerates.

A study of the obscuring-power measurements of fineness and degree of dispersion can also be used to judge the ability of paint mills to grind and incorporate pigments in oil. The quality of the finished paste or paint from any mill can be determined by these tests, and also, the relative fineness of dry grindings may be checked.

Hallett (1) established a relation between hiding power and tinting strength based on the results of twenty different white pigments. Obscuring-power determinations were also made of these same paints used for the work on hiding power. Graphs have been made plotting the relation between obscuring power and tinting strength, and between

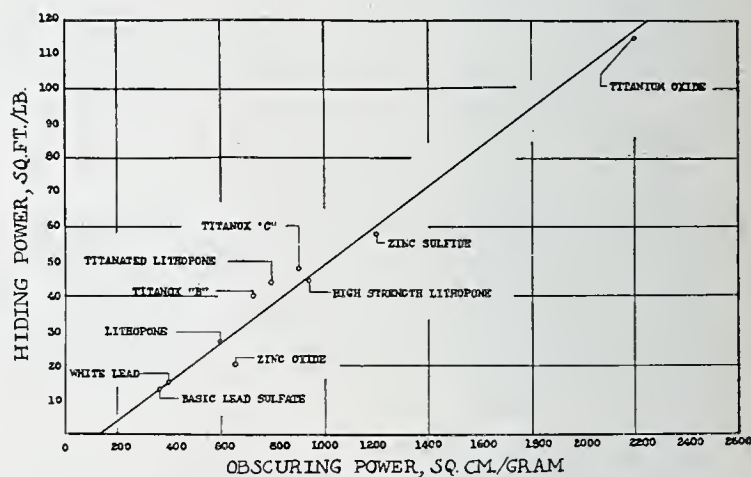


FIGURE 3. RELATION BETWEEN OBSCURING POWER AND HIDING POWER

obscurring power and hiding power, so that the simple obscuring-power test of the paint or pigment can be used to compare one pigment against another, to obtain both hiding power in square feet per pound and the tinting strength on the basis of white lead as 100. The following formulas may be used to convert obscuring power in sq. cm. per gram to hiding power and tinting strength:

$$\text{Hiding power} = \frac{\text{obscurring power} - 140}{17.75}$$

$$\text{Tinting power} = \frac{\text{obscurring power} - 215}{1.68}$$

Figures 2 and 3 more clearly show the relations and the basis for converting one to the other.

Another aid in judging the merit of a pigment is the indication of the presence of sub-microscopic particles. Stutz and Pfund (2) show the effective use of light filters to indicate colloidal fineness. Large particles are more opaque to red than green, and conversely small particles are more transparent to red than green. Therefore, when the obscuring power is lower for red than for green light it indicates the presence of colloidal material. As the value for the red light becomes increasingly less, there is evidence of greater fineness—that is, the average diameter for the sample is probably much smaller than for a product which has only a

slight difference between red and green. Therefore, if both a red and a green filter are used in obtaining the obscuring power, the results can be used to show the presence of colloidal particles.

The obscuring-power test for a paint or paste requires approximately 15 to 20 minutes, and for a dry pigment about 35 minutes. A simple control test of this nature which nets so much information after being calibrated seems invaluable in the paint industry. The new Burgess-Parr turbidimeter just put on the market uses the same principle for measuring turbidity as the one used in developing this work. If this new turbidimeter is properly diaphragmed and a straight-strand galvanometer-type bulb mounted below the base instead of on top of the base, thereby minimizing extraneous

light, then both turbidimeters will be on exactly the same basis and will give the same obscuring-power results.

ACKNOWLEDGMENT

Many thanks for helpful suggestions are due G. O. Hiers under whose supervision the work was developed.

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Analysis of Hydrocarbon Gases

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METHODS for the complete analysis of hydrocarbon gases have already been described by others. In general they involve the complete liquefaction of the gases by means of liquid air or liquid nitrogen. This is followed by fractionation of the liquefied gases. The earlier workers accomplished this by repeated simple distillations. However, in recent years this laborious and relatively ineffective method is being replaced by distillation through low-temperature fractionating columns (1, 7).

The present method is also based primarily on the fractionation of a liquid condensate, but not all the gas is condensed. Liquid air is not required, and solid carbon dioxide and acetone provide all the necessary refrigeration.

The apparatus and manipulation which are described were developed largely from experience gained in the analysis of many gases in this laboratory.

The general procedure will be plain from Figure 3. The original gas is partially condensed by slow passage through a receiver maintained at a constant temperature near -80°C . If the original gas is uniform in composition and if the temperature and pressure of condensation are maintained constant, then the compositions of the condensing liquid and of the uncondensed gas will not change with time. The uncondensed gas is measured and analyzed as described in more detail below. The liquid condensate is measured and then fractionated by means of a low-temperature column into a gas cut, a propane cut, a butane cut, a pentane cut, and residue. These separate cuts are analyzed by the methods indicated in Figure 3 and described in the text. The quantity of each constituent, preferably expressed in moles, having thus been obtained, the composition of the original gas is easily calculated.

PARTIAL CONDENSATION OF GAS

The gas must be thoroughly dried by passing through tube A, Figure 1, filled with dehydrite. Moisture, unless eliminated, will freeze out in receiver B and may stop up the inlet

This procedure for the analysis of hydrocarbon gases is based primarily on the fractionation of a liquid condensate from the gas. However, not all the gas is liquefied, and liquid air is not necessary. Solid carbon dioxide and acetone provide all the refrigeration required.

The analysis of the separate fractions is accomplished largely by methods of standard gas analysis. Diagrams of the procedure and of the necessary apparatus are given. The results from the analysis of a synthetic mixture of pure hydrocarbons are shown and an illustration of the practical application of the method is given.

tube. Further, it will cause trouble in the subsequent fractionation of the liquid condensate by freezing in the lines and also by preventing sharp fractionations between the cuts.

The conditions of condensation must be so regulated that the uncondensed gas practically reaches equilibrium with the liquid condensate during their separation. This means that the internal temperature of the graduated receiver B must remain constant and that the gas must not be passed in too

fast. A mush of solid carbon dioxide and acetone will easily maintain a temperature of -78° to -80°C . in the Dewar vessel C. However, if the condensate is formed too rapidly, its heat of condensation may raise the temperature of the liquid several degrees above that of the refrigerant outside. Uncertainty on this point can, of course, be avoided completely by immersing a thermometer in the condensate itself. For the apparatus shown in Figure 1, a rate of gas flow equal to about 0.05 cu. ft. per minute was found to be good practice.

It is essential that the condensation set-up be gas-tight. This can easily be accomplished with reasonable care¹ since it is subjected to only slight pressures, but tightness should never be taken for granted. Before each test, an open-tube manometer should be attached and air blown in to a pressure of about 2 inches (5.08 cm.) of mercury, and shut off. The apparatus should hold this pressure for at least 5 minutes.

FRACTIONATION OF LIQUID CONDENSATE

It must be borne in mind that the condensate contains large proportions of propane and other substances which at ordinary temperatures are gases and even at -78°C . are highly vola-

¹ Leaks are most frequently found where a glass tube passes through a cork stopper. It is often difficult to find a cork borer of the exact diameter required. The following procedure, first shown to one of the writers by Professor A. A. Morton, is recommended: Bore the hole slightly smaller than required and then gently enlarge it to the required size by a tight roll of fine sand paper (a round file is bad for this purpose). Joints made in this way with good stoppers hold pressure well. If desired they can be covered with collodion.

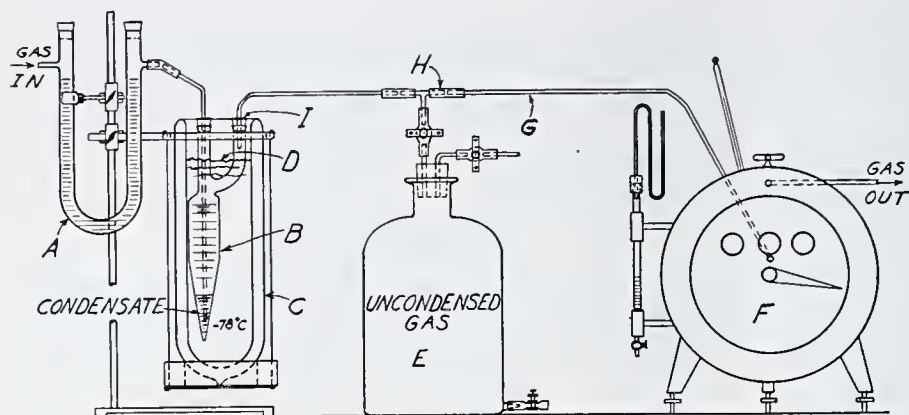


FIGURE 1. APPARATUS FOR PARTIAL CONDENSATION OF GASES

- | | |
|-------------------------------------|------------------|
| A. Dehydrite tube | F. Wet-gas meter |
| B. 100-cc. graduated receiver | G. Glass tubing |
| C. Dewar flask | H. Rubber tubing |
| D. CO ₂ -acetone mixture | I. Cork |
| E. Aspirator bottle | |

tile liquids. Therefore, the fractionating unit, Figure 2, must also be gas-tight or the test will be worthless. It should hold an inside pressure of about 2 inches (5.08 cm.) of mercury for at least 5 minutes.

After the fractionating unit has been proved gas-tight, the head of the column is cooled to about -70°C . by means of solid carbon dioxide and acetone in cup *D*. Next, the condensing tube *B*, of Figure 1, which becomes the distillation flask *B*, in Figure 2, is attached, making sure the joint is gas-tight. During this operation it is still kept in the condensing bath at -80°C . The connection to the gas-collecting bottle *E* is opened and the water levels equalized. Now the condensing bath around tube *B* is removed, and a wrapping of asbestos paper is slipped around its top and the connection to the column. The tube is surrounded by a Dewar flask, 3 by 8 inches (7.62 by 20.32 cm.), half filled with carbon dioxide-acetone mixture. Exact control of the distillation can be obtained by simply lowering or raising the Dewar flask.

The distillation may now proceed. The head temperature is maintained at -70°C . until there is no further increase in the volume of the gas cut. By this time, the reflux is usually established. Now the small graduated receiver *A* is placed in the carbon dioxide-acetone bath, *C*, used previously, and the distillation temperature is allowed to rise slowly to -48°C . Between this temperature and -30°C . practically all the remaining propane-propene is fractionated off and the liquid distillate is practically free from ethane. Next, gas bottle *E* is disconnected, the liquid-distillate receivers changed, and the Dewar flask removed. The temperature will rise slowly to about -10°C . with little distillate showing, but from here to $+10^{\circ}\text{C}$. the butane-butenes appear. The pentane-pentenenes come over between about 25° and 45°C ., but the cut between the pentane and hexane fractions is not so sharp as those between the lower boiling ones. The liquid boiling above 45°C . is left in the flask as residue.

The only precaution necessary in addition to the above directions is that at each temperature all distillate possible be taken off before allowing the temperature to rise. The technic of the entire fractionation can easily be acquired.

The volume of each liquid cut at -80°C . and the volume of the gas cut at room temperature and pressure are recorded for use in the calculations of composition.

ANALYSIS OF FRACTIONS

The operations necessary for the examination of the individual gas and liquid fractions are outlined in Figure 3. In the main, they are ordinary methods of gas analysis, and only features which are exceptional or likely to present difficulties are discussed.

As here outlined, the method determines only paraffinic and

olefinic hydrocarbons and butadiene. However, by using, in addition, certain well-known reagents at appropriate points, it is hoped to extend it to include acetylenes, diolefins, and cyclic hydrocarbons.

UNCONDENSED GAS. The acid gases (carbon dioxide, hydrogen sulfide, and sulfur dioxide) are estimated in the ordinary way by absorption in caustic potash.

Propene is removed by sulfuric acid (87 per cent concentrated). Ethylene is absorbed by bromine, potassium bromide solution, followed by a caustic wash to remove bromine vapors. A separate pipet from that for acid gases is used, since the hypobromite gradually formed here can remove unsaturates as well. Correction must be made for the ethylene which is removed along with the propene by the sulfuric acid. In this absorption, a slow constant decrease in volume per pass is soon reached. This rate is multiplied by the total number of passes, and the resulting volume is subtracted from the apparent propene and added to the ethylene as determined by bromine absorption.

Oxygen is determined by absorption in potassium pyrogallate. The ratio of nitrogen to this is considered to be the same as in ordinary air. This assumption can, however, be in error for the following reasons: (1) The proportions of nitrogen and oxygen in the original gas may not be the same as in air. Thus, the oxygen may have been partly or totally removed, as in a cracking process. (2) Some of the oxygen in the uncondensed gas comes from air evolved from the water over which the gas is collected. The ratio of oxygen to nitrogen in this air is higher than in true air. As the results

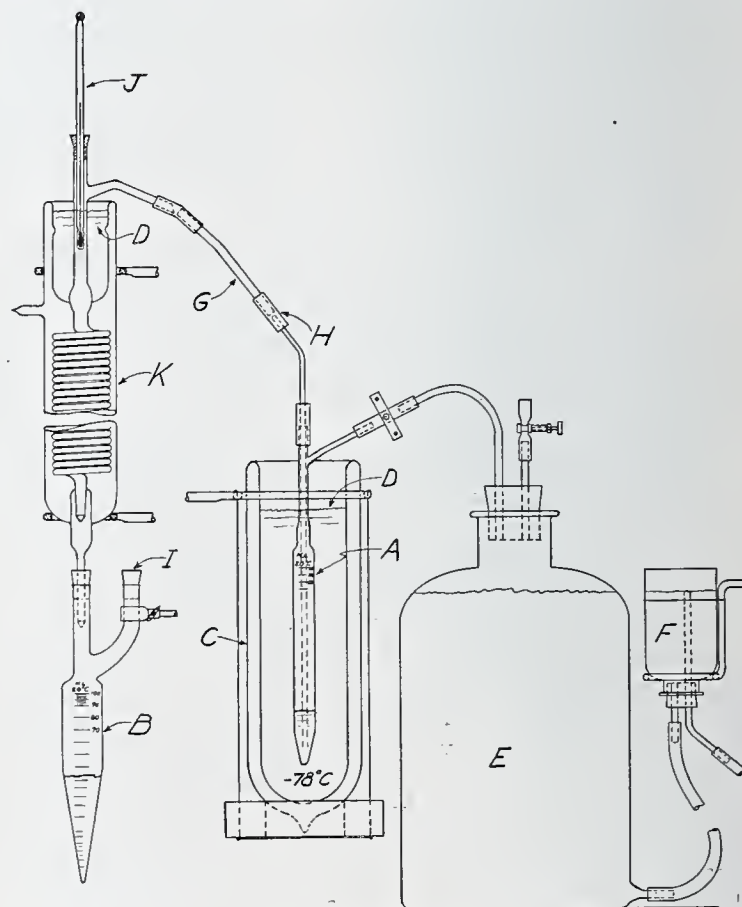


FIGURE 2. APPARATUS FOR FRACTIONATION OF LIQUID CONDENSATE

- | | |
|-------------------------------------|--------------------------------------|
| A. 25-cc. graduated receiver | G. Glass tubing |
| B. 100-cc. graduated receiver | H. Rubber tubing |
| C. Dewar flask | I. Cork |
| D. CO ₂ -acetone mixture | J. Pentane thermometer |
| E. 8-liter aspirator bottle | K. Vacuum-jacketed spiral (35 coils) |
| F. Level equalizer | |

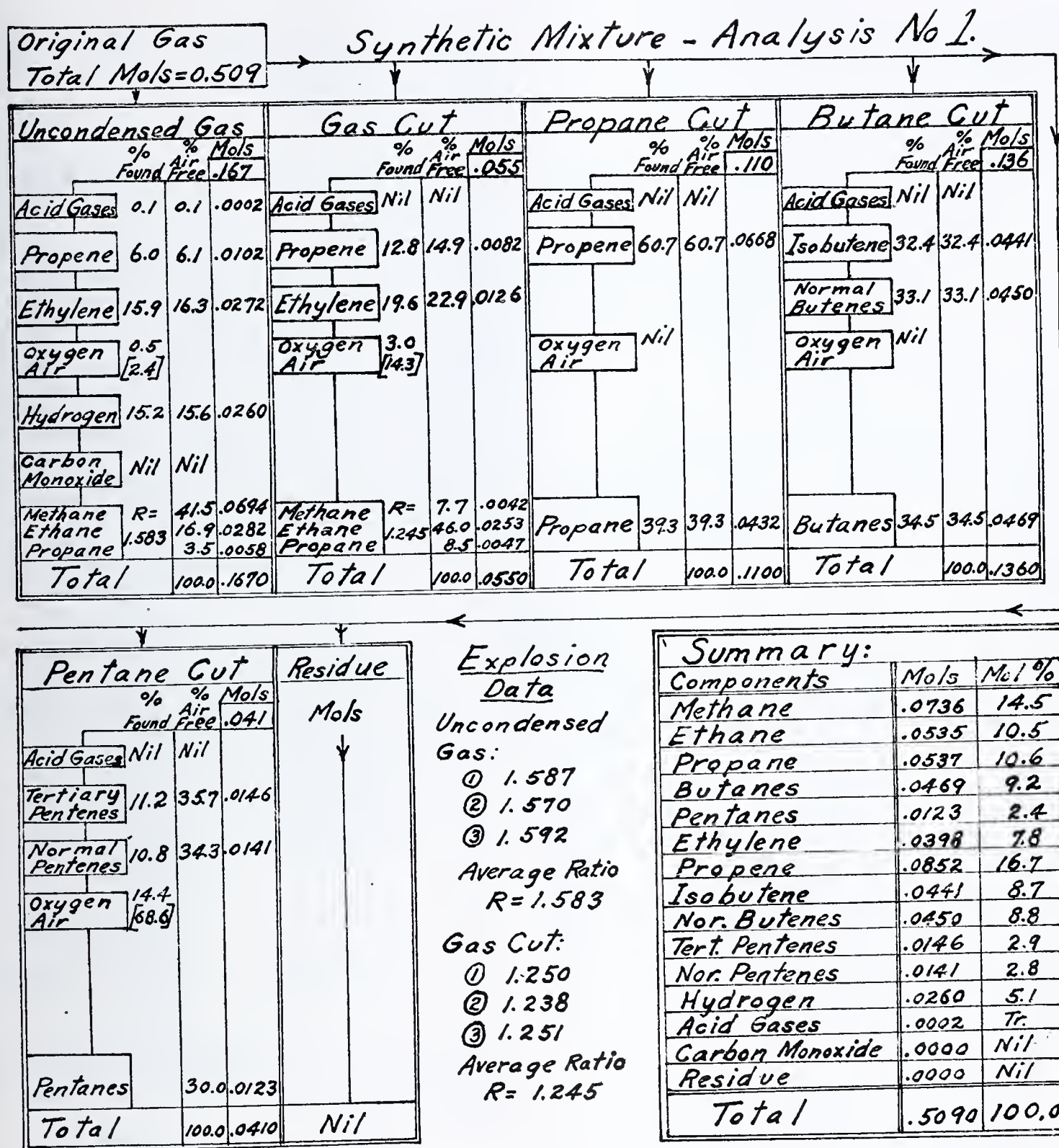


FIGURE 3. OUTLINE FOR ANALYSIS OF HYDROCARBON GASES SHOWING DATA FOR ANALYSIS 1

in Figure 3 illustrate, the errors from this uncertainty in the oxygen-nitrogen ratio have never been great. However, the gases should be analyzed soon after collection to avoid changes in composition due to differences in the solubilities of their components in water.

Hydrogen and carbon monoxide are determined by low-temperature combustion over copper oxide followed by a caustic wash.

If the fractionation was good and if the treatments of the uncondensed-gas fraction up to this point have been thorough, then the residual gas can contain only nitrogen, methane, ethane, and propane. The determination of the proportions of the three paraffinic gases is based on the shrinkage in volume and the volume of carbon dioxide formed on explosion with oxygen. This provides only two equations for three

unknowns. However, one of the unknowns, the fraction of propane, can be independently calculated in two ways.²

1. From the ratio of propene to propane found by analysis of the liquid propane cut. The ratio in the uncondensed gas should be about 1.135 times greater than this [calculated from the ratio of the vapor pressures of propene and propane at -80° C. (6)], and the propene content of the uncondensed gas is known.

2. From the mole fraction of propane in the liquid condensate. The vapor pressure of hydrocarbons from their mixtures are rather accurately proportional to their vapor pressures in the

² These methods for estimating propane in the mixture were developed by one of our associates, V. Schneider, in the Research Laboratory of Applied Chemistry at the Massachusetts Institute of Technology. We also wish to acknowledge his valuable assistance in the development of the present analytical scheme.

pure state and to their mole fractions in the mixture. For this calculation the actual temperature of partial condensation must be determined as discussed above.

The fractions of methane and ethane in the residual saturated gas can be calculated by substituting in the following equations:

If M = fraction by vol. of methane in hydrocarbon part of residual gas
 E = fraction by vol. of ethane
 P = fraction by vol. of propane
 R = $\frac{\text{decrease in vol. on combustion with oxygen}}{\text{vol. of CO}_2 \text{ formed}}$

Then $M = \frac{P(R - 0.5) + 2R - 2.5}{R - 0.5}$

$E = \frac{P(1 - 2R) - R + 2}{R - 0.5}$

or, more simply, $E = 1 - (M + P)$.

GAS CUT. This fraction consists of ethane, ethylene, a lesser amount of methane, and a small quantity of propane and propene. The analysis for these components is carried out as in the case of the uncondensed gas. The oxygen present here can come from only the true air in the column and connections and from the water in the collecting bottle.

PROPANE CUT. This fraction consists of propane and propene only. The liquid volume at -80°C . is recorded, after which the cut is allowed to vaporize completely into an aspirator bottle by water displacement. This can be accomplished without the admission of air, but it is advisable to test for its presence. The propene is determined as shown, and the residue is considered propane. Specific gravity determinations (gas-balloon method) on the entire gaseous fraction have repeatedly checked the values obtained from calculations based on the analysis of the same fraction. Nor does further treatment with bromine water after removing the propene show the presence of ethylene.

BUTANE CUT. This fraction of refinery gases commonly consists of butanes, butenes, and erythrene (1,3-butadiene). The other four carbon-atom hydrocarbons are rarely encountered. It is vaporized over water and analyzed as shown. The isobutene is removed by 63 per cent sulfuric acid and the normal butenes by concentrated acid.

Dobrzanski (5) has pointed out that erythrene is absorbed by 63 per cent sulfuric acid at a rate intermediate between those of isobutene and the normal butenes, and closer to the latter. In experiments with pure gases, no difference was detected in the rates of absorption of 1-butene and erythrene (0.1 cc. from 100 cc. per pass, through 63 per cent sulfuric acid in a bubbling pipet). On the other hand, isobutene was absorbed at the rate of 4.5 cc. per pass (compare 4). The results from analyses of synthetic mixtures of these gases is shown in Table I. Here correction was made for the slow absorption of the normal butene and erythrene, as described above in the separation of ethylene and propene.

TABLE I. ANALYSES OF SYNTHETIC MIXTURES (BUTANE CUT)

MIXTURE	COMPONENTS	VAPOR	
		Taken %	Found %
1	Isobutene	25.9	25.5
	1-Butene	32.7	33.2
	n-Butane	41.4	41.3
2	Isobutene	23.9	23.7
	1-Butene	30.2	37.5
	Erythrene	7.7	
	n-Butane	38.2	38.8

PENTANE CUT. This fraction is well in the gasoline range and should not often occur in a gas. However, it can easily

be analyzed in the vapor state by the following procedure: A measured portion is introduced into a calibrated, partially evacuated aspirator bottle containing a little water. The bottle is allowed to stand under vacuum a short time to evaporate the hydrocarbons completely, and then air is allowed to enter up to atmospheric pressure. The pentane vapors should not exceed 35 per cent of the total gaseous volume. This sample should not be allowed to stand over any considerable volume of water before analysis because of the solubility of the hydrocarbon vapors.

By means of 70 per cent sulfuric acid, the *t*-pentenes (trimethyl ethene and unsymmetrical methyl ethyl ethene) can be separated from the normal pentenes. The results on synthetic mixtures are given in Table II. The procedure adopted here was to pass the gas sample repeatedly and quickly through the acid, in a bubbling pipet, until the absorption per pass was only 0.1 cc. The vapors absorbed up to this point were considered *t*-pentenes. When rational corrections for the absorption of the normal pentenes were made, the results did not check with the known compositions of the mixtures. It will be noticed that isoprene is absorbed with the *t*-pentenes. The behavior of the other pentadienes needs further investigation.

TABLE II. ANALYSES OF SYNTHETIC MIXTURES (PENTANE CUT)

MIXTURE	COMPONENTS	VAPOR	
		Calcd. %	Found %
1	Trimethylethene	50.5	50.4
	Pentene-2	49.5	49.3
2	Trimethylethene	34.5	34.4
	Pentene-2	33.9	34.2
	Normal pentane	31.6	31.4
3	Trimethylethene	16.3	16.4
	Pentene-2	31.9	31.7
	Normal pentane	51.8	51.9
4	Trimethylethene	54.9	54.2
	Pentene-2	30.8	32.0
	Normal pentane	14.3	13.8
5	Trimethylethene	20.9	20.8
	Pentene-2	41.0	41.0
	Normal pentane	38.1	38.2
6	Isoprene	52.0	53.5
	Trimethylethene		
	Pentene-2	24.9	24.1
7	Normal pentane	23.1	22.4
	Isoprene	31.7	32.4
	Trimethylethene		
	Pentene-2	30.5	29.5
	Normal pentane	37.8	38.1

RESIDUE. In the exceptional case where a residue above the pentane fraction was left from the fractionation, its weight was found and its molecular weight either estimated or determined experimentally.

ANALYSES OF SYNTHETIC MIXTURE

To establish the limits of the variations in the values obtained for separate components and to test the accuracy of the method, a 50-liter synthetic mixture of pure hydrocarbons was prepared and analyzed. It was stored in a gasholder of special design, where the space ordinarily occupied by water was largely blocked off by an internal cylinder. The gases, accordingly, contacted with only a minimum quantity of water. Three samples of this mixture were analyzed over a period of 1 week. The results of these analyses and the composition of the synthetic mixture are given in Table III, and the details of the first analysis are shown in Figure 3.

The curves of the three fractionations are given in Figure 4. The standardized-thermometer readings were corrected for stem exposure. In the case of the pentane thermometers used this correction amounted to -3.6°C . in the range of the propane-propenes and to -2.0°C . in that of the butane-butenes.

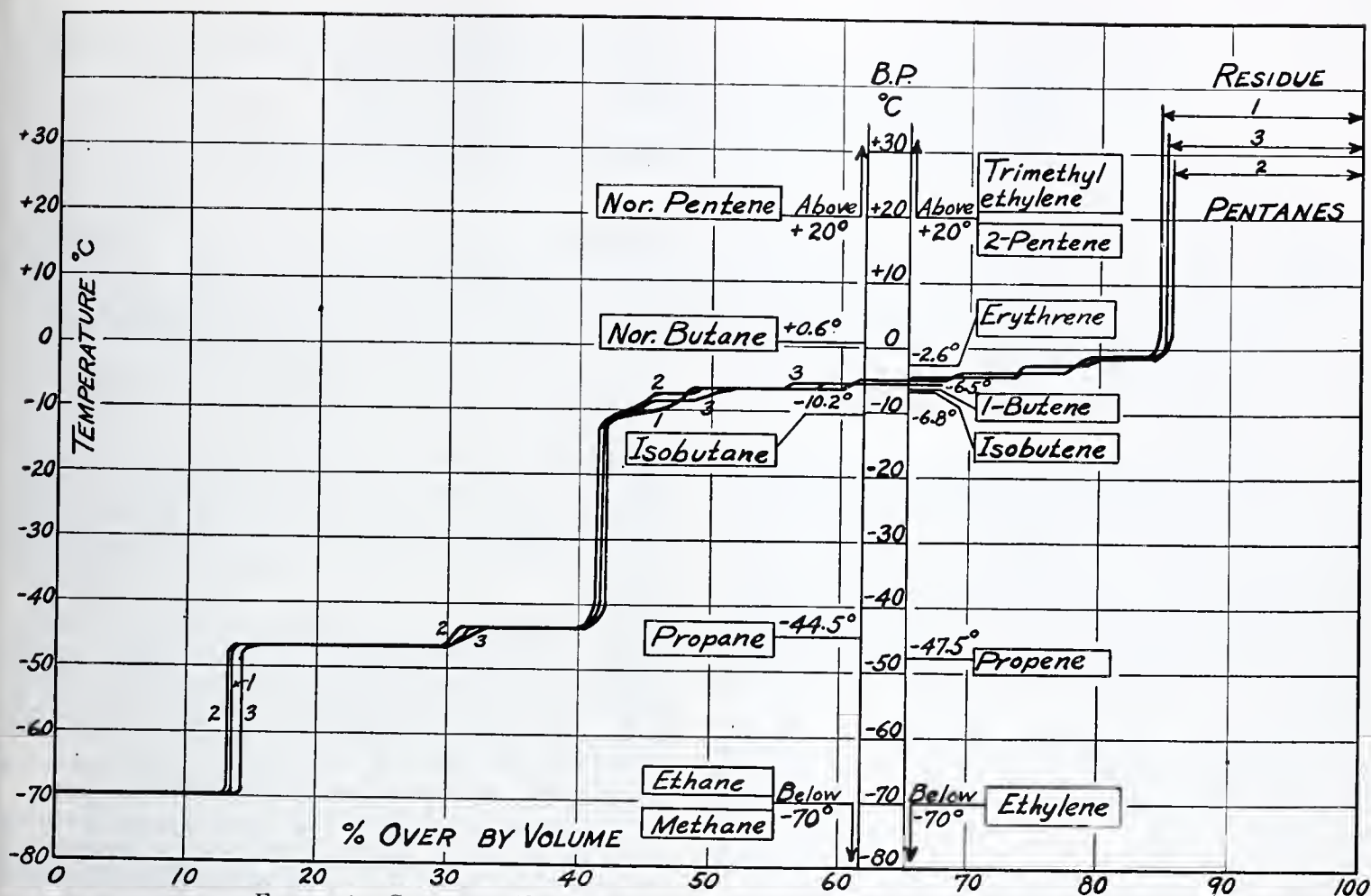


FIGURE 4. CURVES OF FRACTIONATIONS OF SYNTHETIC HYDROCARBON MIXTURE

TABLE III. ANALYSIS OF SYNTHETIC MIXTURE

COMPONENTS	AMOUNT FOUND				AMOUNT TAKEN
	1 Mole %	2 Mole %	3 Mole %	Av. Mole %	
Methane	14.5	15.0	15.1	14.9	14.8
Ethane	10.5	10.7	11.0	10.7	10.8
Propane	10.6	10.1	10.3	10.3	9.9
Isobutane }	9.2	9.6	9.4	9.4	{ 4.3
n-Butane }	2.4	2.5	2.5	2.5	{ 5.0
n-Pentane }					{ 2.5
Ethylene	7.8	7.4	7.7	7.6	7.7
Propene	16.7	16.4	16.3	16.5	16.8
Isobutene	8.7	8.8	8.5	8.7	8.6
n-Butene }	8.8	9.2	8.8	8.9	{ 7.6
Butadiene }	2.9	2.6	2.6	2.7	{ 1.5
t-Pentene }	2.8	2.7	2.7	2.7	{ 2.7
n-Pentene }					{ 2.6
Hydrogen	5.1	5.0	5.1	5.1	5.2
Acid gases	Trace	Trace	Trace	Trace	None
Carbon monoxide	None	None	None	None	None
Total	100.0	100.0	100.0	100.0	100.0

EFFECTIVENESS OF GASOLINE STABILIZER

Analytical methods for hydrocarbon gases are powerful tools for research in organic chemistry. Their practical utility can be illustrated by data from an actual test on a "stabilizer" in a petroleum refinery. Crude cracked gasoline contains considerable quantities of butanes and butenes, propane, and other lighter hydrocarbon gases. It is desirable that the finished gasoline retain a certain amount of butane-butenes, but it should be completely freed from the other gases. This is accomplished in the stabilizer—a high-pressure fractionating tower. Table IV gives the results of analyses (unstabilized gasoline, stabilized gasoline, and exit gas from stabilizer) made to test the effectiveness of a plant unit under experimental conditions. The results show that these conditions would not be satisfactory because the stabilized gasoline contained 2.5 molar per cent (1.1 per cent by weight) of propane-propene.

The results also prove the reliability of the analyses, as the following considerations show. In this particular case, both

stabilized and unstabilized gasolines had the same end point and the gas contained no pentane. This shows that no pentane or residue was lost from the gasoline in the stabilizer. Accordingly, if the molar compositions of both gasolines are tabulated on a basis where the pentanes and residue in each are equal (100 parts), columns A and B, Table IV, then the differences should give the molar proportions of ethane, etc., propane, and butane removed as gas. From these, the composition of the exit gas from the stabilizer, column C, is easily calculated. This agrees well with the composition actually found by analysis, column D.

TABLE IV. RESULTS OF ANALYSES TO CHECK EFFECTIVENESS OF GASOLINE STABILIZER

COMPONENTS	A. UNSTA- BILIZED GASOLINE	B. STA- BILIZED GASOLINE	EXIT GAS		
			A - B	C	D
			Calcd.	Calcd.	Found
	<i>Molar pts.</i>	<i>Molar pts.</i>	<i>Molar pts.</i>	<i>Mol. or vol. %</i>	<i>Vol. %</i>
Ethane, ethylene, etc.	2.29	Trace	2.29	29.6	29.2
Propane, propene	7.37	2.98	4.39	56.7	58.0
Butane, butene	17.42	16.36	1.06	13.7	12.8
Pentane, pentene, and residue	100.00	100.00			
Total	127.08	119.34		100.0	100.0

The fractionating column and accessories described in this article can be purchased from E. Machlett and Son, 50 William St., Long Island City, N. Y.

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RECEIVED August 24, 1931. Presented before the Division of Petroleum Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931.

An Anti-Foam Stillhead

C. W. EDDY, Bureau of Chemistry and Soils, Los Angeles, Calif.

MANY liquids which show a tendency to foam under distillation at atmospheric pressures can be controlled by the addition of a small quantity of amyl, capryl, or some other alcohol of high molecular weight. Even under slightly reduced pressure these alcohols can be used to good advantage but, when pressures of 1 to 2 mm. or less are used, their value as foam preventers is greatly reduced, if not entirely lost.

An experiment conducted recently by the writer required that a solution having foaming tendencies be distilled at a pressure of from 1 to 2 mm. to avoid decomposition. The apparatus used for the distillation was a 2-gallon, steam-jacketed, hemispherical, glass-domed still, surmounted by a short distilling head, which in turn was attached to the usual condenser arrangement. The ordinary short distilling head permitted only slow distillation with no aid in fractionating the abundant foam produced by the liquid when distillation was in progress.

The apparatus of Dupont and Dubourg (1) for distilling saponins under reduced pressure was tried but without success. Lehnert (3) used a distillation apparatus to separate gases from liquids, but from the description it appears improbable that it could be used very effectively for vacuum distillation purposes with liquids exhibiting high foaming tendencies.

Two large anti-foam glass stillheads were made according to the general idea previously published by the author (2). In one, the foam chamber was placed upright (Figure 1), and in the other, the chamber was placed at an angle of 20 degrees (Figure 2) with the horizontal, or 70 degrees with respect to the center foam return.

depends upon the kind of stillhead used and upon the position of the condenser which accompanies the still. The tube *B* is added to accommodate a capillary tube for regulating pressures, if necessary. A thermometer can be placed in *C* to determine the temperature of the distilling liquid.

When the still is in operation, the foam passing up the large side arm, *D*, must contain enough liquid to carry the foam down the center tube, *E*, the lower end of which is always below the surface of the liquid in the vacuum pan, preferably within a few millimeters from the bottom of the pan. This liquid-foam ratio can easily be controlled by the temperature and pressure within the vacuum pan. Uncondensed vapors passing through side arm *A* are condensed in any satisfactory condenser.

With solutions having a low surface tension—e. g., alcohol solutions—the upright stillhead gave better results, whereas with solutions having high surface tensions—e. g., sugar solutions—the horizontal stillhead gave better results. Variations between these two positions may be found advantageous in distilling special solutions, but for the majority of foaming solutions, the horizontal stillhead will be very satisfactory.

A satisfactory anti-foam stillhead for experimental purposes which can be quickly assembled without any glass-blowing may be made by replacing the foam chamber with an ordinary large glass adapter, and the two side arms, *A* and *D*, by glass tubes of proportional sizes. A two-hole stopper in the top of the distilling flask carries both the small liquid-foam return tube, *E*, and the larger vapor tube, *D*.

A more satisfactory separation of the liquid from the foam is accomplished if considerable foaming occurs, as the high

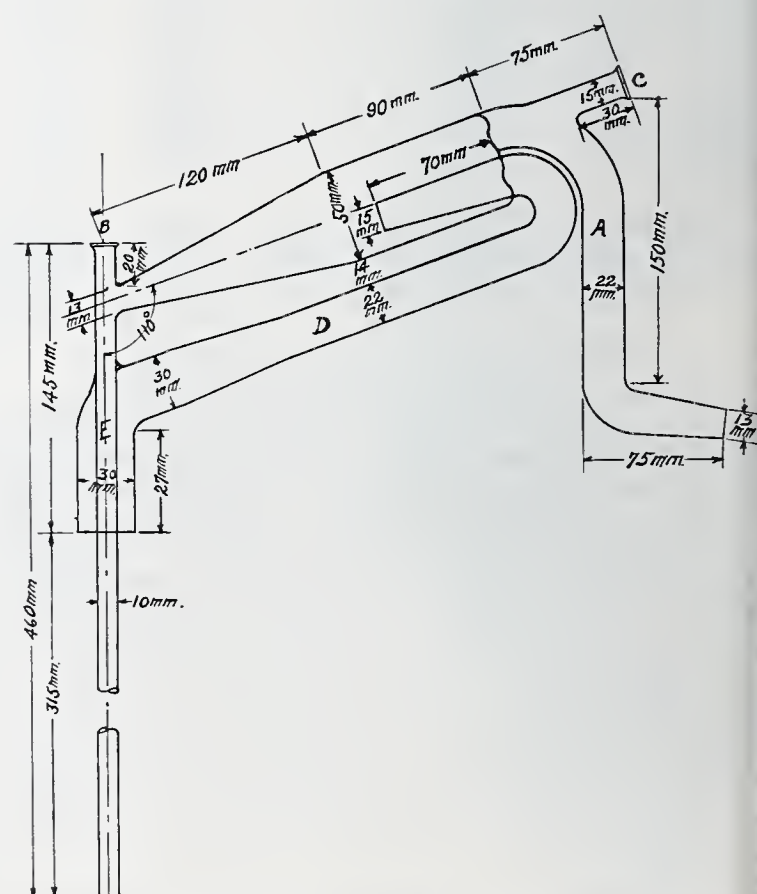
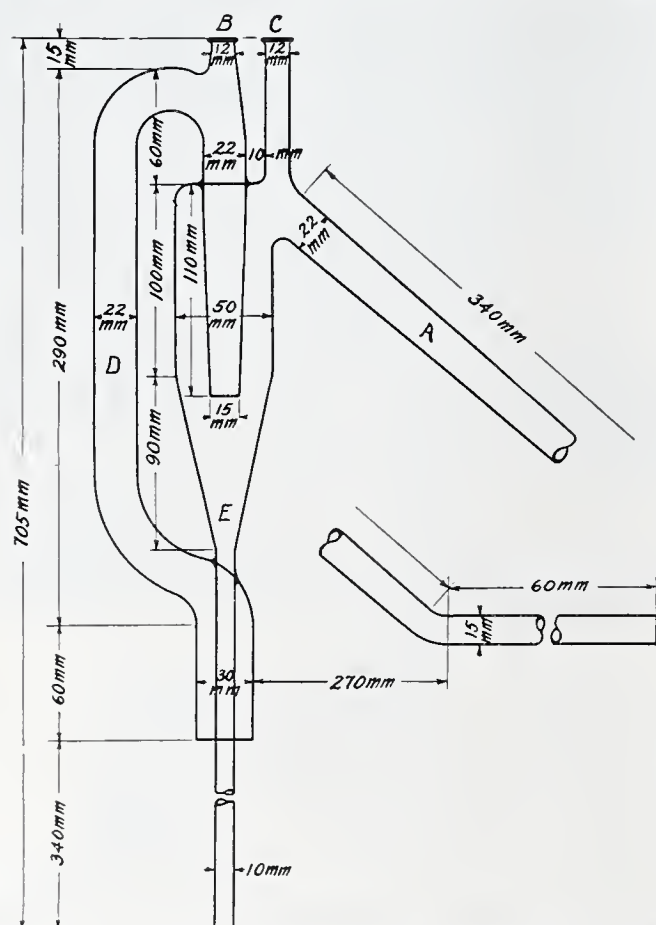


FIGURE 1. ANTI-FOAM STILLHEAD WITH UPRIGHT CHAMBER

FIGURE 2. ANTI-FOAM STILLHEAD WITH CHAMBER AT ANGLE

velocity produced by the tube within the foam chamber forces the liquid-foam mixture down the center tube below the surface of the liquid. In view of the foam reflux action, fractionation is produced to some extent. As a result of numerous runs on solutions having foaming tendencies, the time for ordinary distillation could be reduced one-half to three-fourths by the use of the stillhead described.

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RECEIVED January 7, 1932. Contribution 122, Food Research Division, Bureau of Chemistry and Soils, U. S. Department of Agriculture.

Laboratory Furnace for High Temperatures

HAROLD SIMMONS BOOTH AND ROLAND WARD, Western Reserve University, Cleveland, Ohio

FOR the studies of reactions up to 1000°C . a laboratory electric muffle using a metal resistance wire is quite easily constructed. Above 1000°C ., however, the difficulties of obtaining a controlled temperature increase enormously.

In connection with decomposition studies at high temperatures, it became necessary to devise and build a furnace capable of maintaining a temperature constant to $\pm 5^{\circ}$ in the range 1000° to 1500°C . Although a platinum wound resistance furnace is possible for such temperatures, the cost of

platinum wire for a muffle is almost prohibitive. For this temperature range "Globar" heating elements (silicon carbide resistance rods) obtained from the Global Corporation, Niagara Falls, N. Y., were found to be most satisfactory. After experimentation, the furnace as shown in the plan and side elevation in Figure 1 was devised and built.

It is built in a sheet-iron shell 0.063 inch (0.16 cm.) thick, with bottom and sides bent from one continuous piece into the shape of a sharp-cornered U. This shell is placed on a suitably insulated support and the front and back enclosed by sheets of transite 0.5 inch (1.27 cm.) thick.

Insulation is the most important feature in the construction of a high-temperature furnace. Super X slabs (a coarse asbestos) were used for the layer just inside the transite and the iron shell,

shown in Figure 1, were then mounted in the furnace. (For a description of the terminal mounting and heating elements see Bulletins A and B of the Globar Corporation, Niagara Falls, N. Y.)

For the higher temperatures, an alundum roof (cast from Alundum Cement R. A. 162) in the heating chamber gave trouble by sagging. A slab of sillimanite 0.567 inch (1.44 cm.) thick (furnished by the Champion Porcelain Company, Detroit, Mich.) was found to withstand perfectly the highest temperatures attained in the furnace, and was adopted. After the roof was in place, the insulating material was built up on top of it in the order described and a sheet-iron top covered the whole, serving to hold the two sides together.

The heating elements were connected in series, four elements being used, two on each side of the heating chamber. The furnace operates on a 220-volt current. The temperature was controlled by suitable rheostats connected in series with the elements.

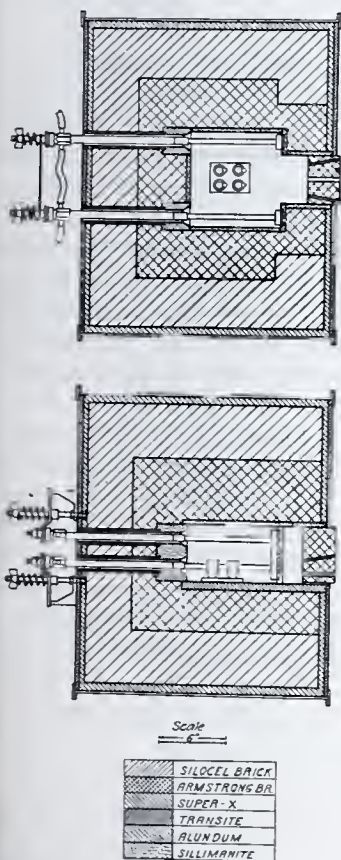


FIGURE 1. LABORATORY GLO-BAR FURNACE

since they pack closely and are an excellent preventive for loss of heat by convection. This layer was about 1.25 inches (3.17 cm.) thick. The second layer 4.5 inches (11.43 cm.) thick, inside of this, consisted of Sil-O-Cel bricks. These bricks have excellent insulating qualities but will not withstand direct heat. The third inner layer surrounding the heating chamber itself consisted of a 4.5-inch (11.43-cm.) layer of Armstrong brick, which is a good refractory and is a fairly good insulator. The floor, side, and back of the heating chamber were made from slabs of alundum 0.5 inch (1.27 cm.) thick, cast from Alundum Cement R. A. 162. The terminal mountings and the heating elements, as

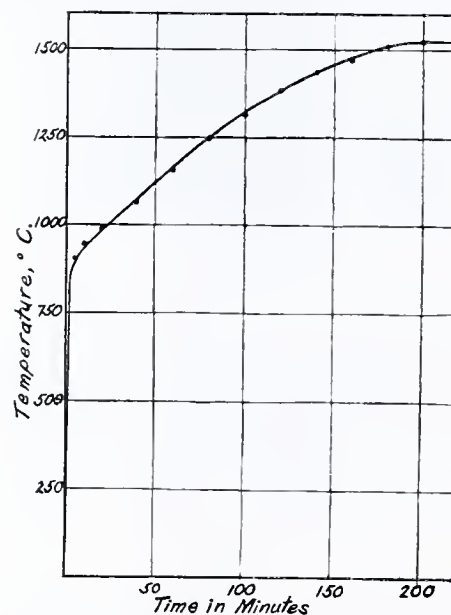


FIGURE 2. HEATING CURVE OF LABORATORY GLO-BAR FURNACE USING 0.5-INCH ELEMENTS

For temperatures from 1000° to 1260°C . it was found convenient to use the 8 by 0.375 inch (20.32 by 0.953 cm.) "Globar" elements (55 volts, 20 amperes), and for higher temperatures the 8 by 0.5 inch (20.32 by 1.27 cm.) "Globar" elements (40 volts, 27 amperes). The temperature was observed by an optical pyrometer and it was found that the light emission of the "Globar" elements increased with age—a factor which must be kept in mind when measuring temperatures of a "Globar" furnace.

In Figure 2 is plotted the heating curve for the 0.5-inch "Globar" elements. The maximum temperature attainable

with no resistance in the line was 1525°C . and was reached after 3 hours. Higher temperatures could be obtained by the use of larger elements, but one is limited by the melting

point of the refractories. The atmosphere of the furnace chamber was found to be slightly oxidizing.

RECEIVED December 21, 1931.

Photographic Records of Vitamin D Line Tests

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A RAPID and economical method developed in this laboratory for obtaining photographs of vitamin D line tests has proved valuable as a means of permanently recording the results, as well as for illustrating published reports (1, 3).

The apparatus illustrated in Figure 1 consists of a small camera designed for direct attachment to the microscope stand. Focusing for a fixed magnification is accomplished through manipulation of the coarse adjustment of the microscope alone. Cameras of this type, differing considerably in certain optical and mechanical refinements, are made by at least two manufacturers (Carl Zeiss, Inc., and E. Leitz, Inc.).

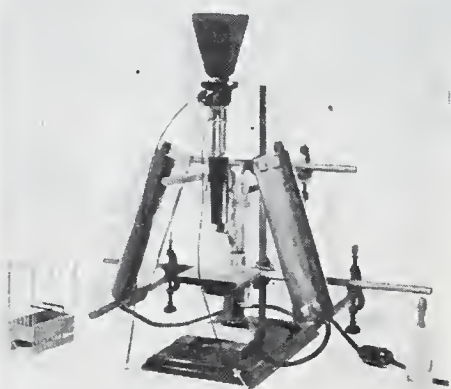


FIGURE 1. PHOTOGRAPHING APPARATUS

By use of an objective of $1\times$ to $2\times$ magnification an image is obtained on a 4.5 by 6 cm. plate of approximately $5\times$ magnification. This degree of enlargement permits the recording of one line test on each plate of sufficient magnification for precise interpretation. A plate of this size also has the advantage of economy both in cost of materials and in storage space.

Incident illumination is provided by two Mazda, tubular, projection lamps (110 volts, 165 watts) mounted in porcelain-lined, show-case reflectors. With this illumination, fully exposed negatives are obtained on panchromatic plates with exposures of from 1 to 3 seconds.

The staining procedure followed in this laboratory conforms in general with the McCollum technic for the vitamin D line test (2). The animals are killed, and a radius is removed from each and cleaned at once. The distal end of the bone is sectioned through the center on a plane parallel with the flat surface where the distal ends of radius and ulna articulate. The two halves of the bone are at once immersed in water for

about 15 minutes, or while an entire series of bones is being prepared for staining. They are then immersed for 1 minute in 1.5 per cent silver nitrate solution, after which they are washed through two changes of distilled water to remove excess silver nitrate. The bones are then exposed in water to daylight or direct sunlight just long enough to develop a delicate straining of the calcified areas without darkening or yellowing the softer tissues. Descriptive records are then made, and the stained bones are stored in water in the dark until photographed. Undue delay in photographing often leads to difficulties, owing to degradation in contrasts through discoloration or unequal swelling of the cut surface.

For photographing, the bone is placed in the center of a 2-inch (5.08-cm.) watch glass and covered with a square cover slip. A sufficient quantity of boiled distilled water is run under the cover glass to just fill the space beneath it. Care must be exercised to avoid the inclusion of minute bubbles between the cover glass and the stained surface of the bone. A black background for the photograph is obtained by lowering the condenser and covering the under side of the stage with black paper from the wrappings of photographic plates. If the stained surface of the bone has become discolored through long standing or over-exposure to light, a better rendering of the calcified structure is ensured by interposing a suitable filter at some position between the object and the plate. The unmounted gelatin color filters are useful, as they may easily be trimmed to a suitable size and are not likely to upset the optical arrangement of the system. It has been found desirable in this laboratory to keep a K3 gelatin color filter, or its equivalent, on the upper surface of the objective mount for all photographs of line tests, as this tends to increase the contrast of discolored specimens without detracting from the quality of photographs of bones that are not discolored. If all exposures are made through the filter, estimation of proper exposure time is considerably simplified, because the filter introduces a constant factor in determining the length of the required exposure.

As panchromatic plates are used exclusively, all manipulations in the dark room are carried out in total darkness.

Rapid and uniform treatment of the plates is facilitated by carrying them through the various solutions and washing water in a developing rack carrying 10 or more plates. The plate rack shown in Figure 1, designed after the one used in the British "Dallon" developing tank, was made to carry 10 plates and fits into a container known as a 4 by 5 inch glass fixing box. This type of container is also used for the rinse or hardening bath and fixing solution. The shape of this container contributes to economy in the use of the developing solution and has the added advantage of a glass cover. Proper development is attained by adhering closely to a time and temperature schedule supplied by the plate manufacturer, the time being measured by an interval alarm timer.

The developing solution used is that recommended by the plate manufacturer for high contrast. A quantity of this

¹ Working under fellowship of the National Cottonseed Products Association.

² The long working distance of this objective necessitated its attachment to the lower end of the draw tube of the microscope illustrated in Figure 1

solution sufficient for several months' work, made up in twice the concentration used for developing, is stored in pint bottles.

The photographs reproduce well either in half-tone or lantern slides, and they enlarge satisfactorily to several diameters. The procedure described can be successfully followed with little practice, and satisfactory records may be rapidly produced by technicians with little knowledge of the principles of photography.

A modification may be made in the foregoing procedure which permits the bone section to be photographed by transmitted instead of reflected light. This modification involves a clearing procedure commonly used in the preparation of histological sections. After staining and washing the bone section as described before, it is dehydrated by successive

15-minute immersions in 50 per cent, 95 per cent, and absolute alcohol. The section then transferred to xylene will "clear," or become translucent, and may be photographed in xylene by means of a substage light source. Although this method may improve the rendering of structural details in some specimens, the results do not, in general, justify the additional time required when only laboratory records are desired.

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An Apparatus for Electrodialysis

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MOST of the schemes for electrodialysis which have been described in the literature require special forms of apparatus which are often expensive and the parts difficult to replace. They usually consist of a cell of three chambers made of glass, earthenware, or rubber, and separated by membranes of various material such as pig bladder, collodion, parchment, parchment impregnated with gelatin, albumin, hemoglobin, and other proteins, and more recently membranes of cellophane.

The most widely used apparatus for electrodialysis is probably that of Pauli (10). It is a three-chambered glass cell fitted with electrodes of platinum or silver gauze, or graphite, and is obtainable on the market (Fritz Köhler, Leipzig). Other cells have been described by various workers in several papers appearing, for the most part, in the *Biochemische und Kolloid Zeitschriften* (1, 2, 6, 9).

Reviews of the work done with electrodialysis in colloidal and biological chemistry have been given by Dhéré (4), Rheinboldt (13), Reiner (11), and Reitstötter (12). The theory of electrodialysis has been considered by these workers, by Ettisch (5) and Bradfield (3), and by others. Ettisch and his co-workers (5) have pointed out several dangers which may occur in the electrodialysis of blood serum. These include the possibility of temperature increases in the dialyzing liquid owing to the resistance of the cell to the passage of the electric current, and a tendency to precipitation of the proteins with the removal of the electrolytes and the changes in reaction which may take place during electrodialysis.

Figure 1 illustrates a simple scheme for electrodialysis, which is very efficient and satisfactory for ridding colloidal and other solutions of electrolytes in a minimum of time. The apparatus is simple and easily constructed at a small cost from material available in almost any biochemical laboratory.

The semi-permeable membranes consist of 2 Schleicher and Schüll parchment diffusion thimbles. The smaller inner thimble (1.6 by 10 cm.) contains an inlet and outlet tube for water and an electrode made of a strip of platinum sealed in a glass tube with a little mercury to make contact with the electric wire which is shoved down the tube. These three glass tubes pass through a rubber stopper which fits the smaller thimble after it has been soaked in water. The second and larger thimble (4 by 10 cm.) contains the material to be dialyzed (about 50 cc.) and is fitted with a rubber stopper with a hole large enough for the smaller thimble to fit neatly into it.

The diffusion thimbles, thus mounted, are clamped into

place so as to dip into a beaker which contains a pool of mercury in the bottom to act as the cathode. A glass tube runs down the inside of the beaker into the mercury and is held in place by a piece of adhesive tape stuck to the side of the beaker. Through this tube, which must be sufficiently wide, an electric wire can be pushed down to make contact with the mercury. The inlet tube for water is connected by means of a rubber tube to the tap or distilled-water bottle. When

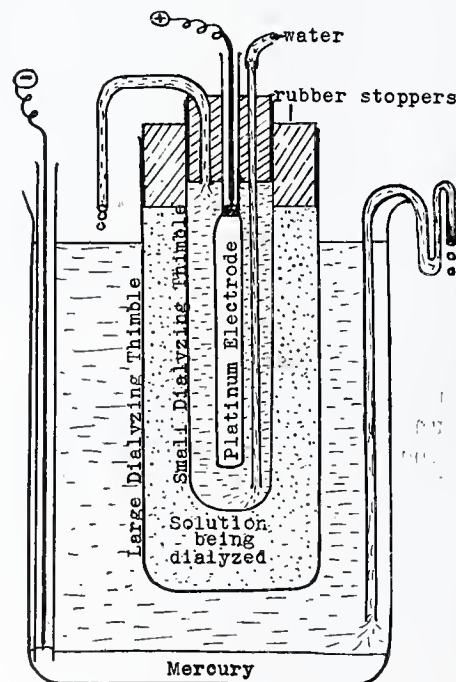


FIGURE 1. DIAGRAM OF APPARATUS

flowing, the water passes through the small thimble and drips into the beaker which, when full, siphons over to a constant level through the overflow tube, as illustrated.

The electric current is passed by means of two leads dipping into their respective bits of mercury, the first making connection with the platinum anode and the second with the pool of mercury cathode. The amount of current passed is conveniently controlled by means of lamps interposed in series, parallel. Under the influence of the electric current, the ions of the electrolytes in the material to be dialyzed are carried to the electrode chambers, where they are washed away by the running water. The dangers referred to above are best avoided by passing a fairly weak current of electricity and by

ensuring that a fairly rapid stream of water passes through the electrode chambers at all times.

The apparatus has proved to be very useful in biochemical procedures. As an example, it was desired to free some aqueous extracts of certain tissues of their inorganic phosphate. It was found that phosphate ion could be reduced to the limits of the method of testing in 2 or 3 hours, whereas it took 48 or more hours to accomplish this against running water in an ordinary cellophane sack.

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Factors Affecting Quantitative Determination of Lignin by 72 Per Cent Sulfuric Acid Method

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A MODIFICATION of the Ost and Wilkening (3) method for the determination of lignin was published by Mahood (2) of the Forest Products Laboratory in 1922. The modified method was designed for the quantitative determination of lignin in wood. Since its publication, Mahood's method has been modified at various times. The need for changes became necessary soon after 1922, when such materials as Cross and Bevan cellulose, chemical pulps, and flax were analyzed for their lignin content. More recently the need for additional changes became apparent when Sherrard and Harris (4) found that slightly elevated temperatures alter the physical and the chemical nature of lignin prepared by the 72 per cent sulfuric acid method.

These modifications may be classified under the following headings: (1) treatment of samples with alcohol-benzene; (2) ratio of acid to sample; (3) extraction of the sample with hot water; (4) duration of contact of sample with 72 per cent sulfuric acid; (5) temperature of the mixture containing 72 per cent sulfuric acid and wood; and (6) duration of hydrolysis.

PRETREATMENT OF SAMPLES

To avoid the presence of foreign materials in the lignin residue, pretreatment of the sample is necessary. The oils, resins, fats, and waxes are removed by extracting the sample with a minimum boiling-point solution of alcohol-benzene as recommended by Mahood (2).

Bray, in determining lignin in chemical pulps (1), found the alcohol-benzene extraction unnecessary in most pulps, since any fatty or resinous materials remaining after the pulping process caused no interference with the subsequent lignin determination. Later the extraction was omitted in the determination of lignin in all chemical pulps. Recently it has been found, however, that the extreme difficulty experienced in filtering and washing the lignin residue from sulfite pulps which retain resins and fats may be largely overcome by

A discussion is given of the discovery of additional factors that affect the quantitative determination of lignin in wood. Owing to a knowledge of these factors, the following modifications have been incorporated in the Forest Products Laboratory method for the determination of lignin in wood:

1. *The residue after extraction with alcohol-benzene should be extracted with hot water.*
2. *The concentrated acid-wood mixture should be kept in a bath at 20° C.*
3. *Two hours should be allowed for solution of the carbohydrates in the 72 per cent sulfuric acid.*
4. *The diluted mixture should be hydrolyzed for 4 hours.*

pretreating such pulps with the alcohol-benzene solvent.

RATIO OF ACID TO SAMPLE

As originally adopted by the Forest Products Laboratory, the method specified 12.5 cc. of 72 per cent sulfuric acid per 2 grams of sawdust. That ratio of acid to sample is sufficient, but it requires considerable time for triturating the wood-acid mixture. If the ratio of the acid to the sawdust sample is increased, as advocated later in this paper, the trituration can be accomplished with greater ease and in less time.

Further, when the method is employed for the analysis of chemical pulps, which have a much higher cellulose content than wood, it is found necessary to increase the acid-sample ratio in order to dissolve the carbohydrates (1).

EXTRACTION OF SAMPLE WITH HOT WATER

If the alcohol-benzene extracted residue is extracted with hot water and dried before treating with 72 per cent sulfuric acid, very noticeable effects are observed in some cases, as is shown in Table I. The lignin residue obtained is lighter in color, the yield lower, and filtration and washing facilitated.

Apparently these effects are due to the presence, in some woods, of extractives which are insoluble in alcohol-benzene but soluble in hot water. Further, these extractives are insoluble in sulfuric acid or converted into insoluble products by the acid treatment.

DURATION OF CONTACT OF SAMPLE WITH 72 PER CENT SULFURIC ACID

The time during which the sample and the concentrated acid are in contact has a direct bearing on the quantity of the lignin residue. Time must be allowed for the carbohydrates to dissolve, but continued exposure appears to caramelize some of the dissolved carbohydrate material partially rendering it insoluble. The insoluble material is thus included in

the lignin residue. The amount of partially decomposed carbohydrate material and the color of the lignin residue increases with the time of contact between the sample and the concentrated acid. Relationships between times of exposure of the sample to the concentrated acid and lignin yields are shown in Figure 1. A period of 2 hours has been adopted for the duration of contact of the sample with the 72 per cent sulfuric acid.

TABLE I. EFFECT OF TEMPERATURE AND EXTRACTION WITH HOT WATER ON LIGNIN YIELDS OF FIVE WOODS

SPECIES	TREATMENT WITH ACID ^a FOR 17 HR. AT ROOM TEMP.	TREATMENT WITH ACID ^a FOR 2 HR. AT 20° C.	
		Without hot-water extraction	With hot-water extraction
Sugar maple	23.15	21.40	21.05
	23.50	21.70	21.20
	23.05	21.45	21.10
	23.25	...	21.35
	Av. 23.24	21.52	21.18
White spruce	27.00	26.00	25.90
	27.50	25.95	25.90
	27.70	26.00	25.95
	27.35	26.30	25.85
	Av. 27.39	26.06	25.90
Incense cedar	35.85	34.80	33.85
	36.40	34.25	33.80
	36.25	34.05	33.75
	36.10	34.10	33.25
	Av. 36.15	34.30	33.66
Catalpa	20.32	17.67	17.23
	20.35	18.12	17.32
	20.55	18.04	17.31
	20.38	18.40	17.34
	Av. 20.40	18.06	17.30
Mesquite	30.20	27.95	24.70
	30.35	28.00	24.70
	30.60	27.75	25.10
	30.55	27.15	24.50
	Av. 30.42	27.71	24.75

^a 72 per cent sulfuric acid.

TEMPERATURE OF CONCENTRATED ACID AND WOOD MIXTURE

Room temperature was originally specified for dissolving the cellulosic material in the 72 per cent sulfuric acid. Since there is usually a wide range in room temperatures during the various seasons of the year, and since Sherrard and Harris (4) have found that the amount and the properties of lignin are altered by slight variations in temperature during its isolation, it seemed advisable to study the temperature factor. From the results recorded in Figure 1, it may be noted that the 17-hour treatment of the sample with 72 per cent sulfuric acid indicates that yields from 22.3 to 28.3 per cent are obtained at temperatures ranging from 17° to 35° C. Shorter treatments of 1 and 2 hours at the same temperatures indicate that yields from 21.5 to 22.5 per cent are obtained. The 1-hour treatment shows, as a result of undissolved carbohydrates, a rise in yield in going from 15° to 10° C. The 2-hour treatment at 20° C. has been chosen, therefore, in order to ensure complete solution of the carbohydrates with minimum decomposition. If these conditions are not maintained, lignin yields may be obtained from refined pulps or from Cross and Bevan cellulose which may be due largely to partially decomposed carbohydrates, as shown by Sherrard and Harris (4). Darker color of the lignin as well as increased yields accompany increasing temperatures of the acid-wood mixture.

DURATION OF HYDROLYSIS

After the dissolving of the carbohydrates is completed in the 72 per cent sulfuric acid, enough water is added to the wood-acid mixture to obtain a 3 per cent acid solution. During the dilution, a part of the modified carbohydrates in the form of dextrin-like material is re-precipitated. The mixture must therefore be boiled in order to hydrolyze and render soluble all the carbohydrates and at the same time coagulate the

finely divided insoluble ligneous material so that filtering and washing of the residue may be facilitated.

Working with several woods, it was found that 4 hours are sufficient for the hydrolysis of the carbohydrate portion, giving a clear filtrate. For shorter periods the filtrate from some woods was cloudy and gave a brown residue, whereas some of the woods examined did not require such a long period. Some types of materials to be examined in the future may require even longer periods, in which event the 4-hour period should be modified to suit the conditions.

PROCEDURE FOR DETERMINATION OF LIGNIN IN WOOD

Since it has been shown that certain factors affect the lignin determination, it is suggested that the sulfuric acid method for the determination of lignin in wood be modified to read as follows:

Approximately 2 grams of air-dried sawdust (60 to 80, or 80 to 100 mesh) are weighed in a tared alundum crucible. The crucible and its contents are dried to constant weight at 105° C., cooled, and weighed. The material is then extracted for 4 hours in a Soxhlet apparatus with a minimum boiling solution of alcohol-benzene. The solvent is removed by suction, the residue washed with alcohol by suction to remove the benzene, and then extracted with 400 cc. of hot water in a water bath for 3 hours, filtered, washed with hot water, then with alcohol, and finally dried. (Washing the

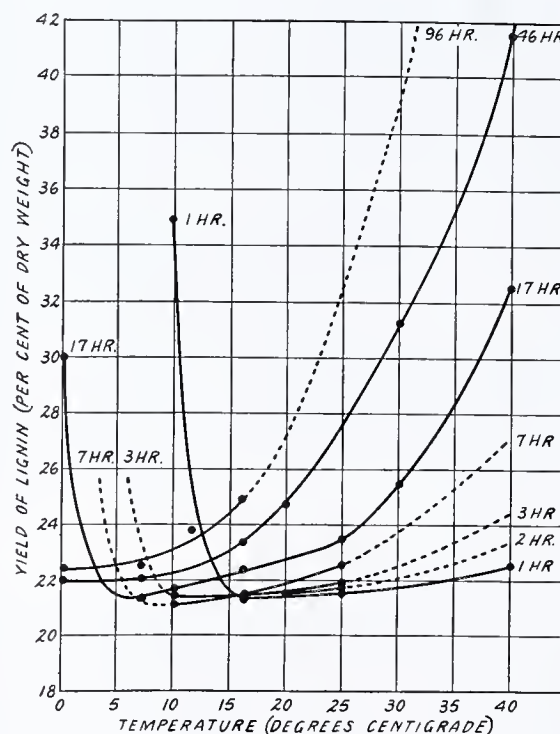


FIGURE 1. EFFECT OF TIME AND TEMPERATURE ON LIGNIN YIELDS IN SUGAR MAPLE WITH 72 PER CENT SULFURIC ACID

residue with alcohol aids in the removal of the sawdust from the crucible after drying.) The dried residue is transferred to a glass-stoppered weighing bottle, and is well mixed with 25 cc. of 72 per cent sulfuric acid at 20° C., and maintained at that temperature for 2 hours. The resulting mixture is transferred to an Erlenmeyer flask, diluted with water to make a 3 per cent acid solution, and then boiled for 4 hours under a reflux condenser. The hydrolyzed residue is filtered on a tared alundum crucible, washed free of acid by means of hot water, dried, and weighed. The lignin content is calculated on the basis of the oven-dry sample.

In case a correction for ash is desired, transfer the lignin residue to a tared platinum dish and ash in the usual way.

In the determination of lignin in chemical pulps, 40 cc. of 72 per cent sulfuric acid should be used for dissolving the

carbohydrates present in a 2-gram sample. The water extraction may be omitted with all chemical pulps and the alcohol benzene may be omitted with alkaline-cooked pulps.

If large quantities of lignin are prepared at one time, it is difficult to control the temperatures developed during the mixing of the acid and the sawdust. It is advisable, therefore, to use a lower concentration of acid and mix it with the sawdust at a lower temperature than specified above. Sherrard and Harris (4) have found that a 70 per cent sulfuric acid mixed with sawdust at 10° C. is satisfactory.

Results obtained from lignin determinations in several woods according to the foregoing revised method are recorded in the last column of Table I. The effect of tempera-

ture on the lignin yields may be noted by comparing columns 1 and 2; the effect of hot-water extraction, by comparing columns 2 and 3.

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New Test for Fat Aldehydes Resulting from Oxidation of Fats and Oils

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OXIDATION of fats and oils leads to the development of tallowy odors and flavors whose measurement is exceedingly difficult, being subject to the senses of smell and taste which vary greatly in different people. Numerous attempts have been made to measure the degree of oxidation by determining the products of oxidation.

The most widely used test for tallowiness in fats, including fatty oils, is the Kreis test. This test depends on a color reaction between phloroglucinol and the oxidized fat. A known amount of fat is shaken vigorously for 30 seconds in a test tube with concentrated hydrochloric acid. A 0.1 per cent solution of phloroglucinol in ether is added and the mixture is again shaken. It is then allowed to stand. If the fat is tallowy, a red or pink color appears in the acid layer.

Kerr (4) stated in 1918 that the Kreis test is only roughly proportional to the rancidity. He agrees with Winkel (9) that it is too delicate and not specific. The expression "rancidity" is used by these investigators in a broad sense which covers other flavors than those due to oxidation. This has led to confusion among other workers who have tried to apply the Kreis test to all types of deterioration in fats and oils.

In recording the results of the Kreis test, it has been customary to designate each as positive or negative. This is not entirely satisfactory, for it fails to take into account the fact that the same degree of oxidation in different fats and oils may result in the formation of oxidation products widely differing in character, with corresponding variations in flavor and odor. It is therefore important to judge each type of fat or oil on its own merits. In comparing flavor scores with the readings of any test for oxidation products, it is important to have for each fat or oil an individual scale, varying according to the use for which the fat or oil is intended.

Holm and Greenbank (2) have shown that the Kreis test can be applied in a quantitative way when relatively large

Oxidation of edible fats and oils leads to tallowy flavors and odors. These are considered to be due to the formation of various aldehydes. A new test for fat aldehydes has been developed, and experimental data are presented to show the best composition of the new reagent and the method of procedure which will give the optimum color effect. The new rosaniline reagent is over twenty times as sensitive as the Kreis test or the Schiff reagent. It is specific for fatty glyceride aldehydes. The results of the new test are expressed in arbitrary specific color units which are called "fat aldehyde values." Special applications are given. Oxidation tests with butter fat at 50° C. gave correlation between the amount of oxygen absorbed and the fat aldehyde value.

amounts of oxygen are absorbed by butter fat at a temperature of 95° C. It would not be quite safe to assume that the same quantitative relationships exist at lower temperatures and during the early stages of oxidation.

Powick (6) and later Munding (5) in Germany have done a great deal of work on the Kreis test. Powick applied the test to a large number of compounds found in oxidized fats and oils. The only one which gave the characteristic color with phloroglucinol was epihydrinaldehyde. The formation of this aldehyde from oleic acid by a complicated series of

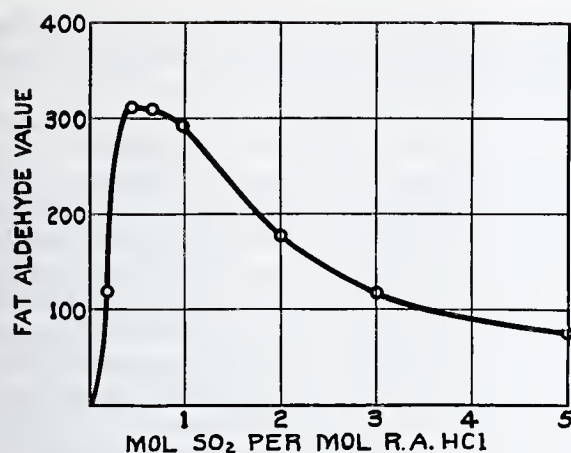
reactions is suggested by Powick. Perhaps the fact that the color reaction of the Kreis test depends on the presence of one special aldehyde explains why this test is often unreliable.

Richardson (7), as chairman of a Kreis test committee, reports on the use of the test on wintered cottonseed oil. He prepared six samples of this oil with varying exposures to the air. These samples were sent to three different laboratories to be tested according to Kerr's directions. The conclusion was that the average grading of the samples by this method failed to disclose any correlation between intensity of the Kreis test and rancidity as judged by flavors.

Von Fellenberg (1) in Switzerland and Inichof and Schoschine (3) in Russia used the Schiff reagent as a test for aldehydes in fats and oils. The Schiff reagent was the customary yellow solution which is made by adding a sodium sulfite or bisulfite solution and hydrochloric acid to a fuchsine solution. Von Fellenberg's modification is the least acid and also the most sensitive. Munding states that the von Fellenberg test is better than the Kreis test, but neither of these is as sensitive as an organoleptic test when applied to butter fat.

EXPERIMENTAL PROCEDURE

The purpose of the present investigation is to develop a sensitive and reliable test for measuring fat aldehydes. The

FIGURE 1. EFFECT OF SO₂ CONCENTRATION

Schiff reagent seemed the most promising starting point. Oxidation of fats undoubtedly produces aldehydes, which will to some extent respond to the Schiff reagent.

A tallowy colorless sample of butter fat which had absorbed about 0.7 cc. of oxygen per gram of fat was used. One gram was dissolved in 100 cc. of petroleum ether (b. p. 50° to 100° C.). When this fat solution was shaken with the ordinary yellow Schiff reagent, a color reaction took place which changed the aqueous solution from yellow to orange-red. The petroleum ether solution was also colored yellowish red, but not so much as the aqueous solution. A very heavy dark red emulsion formed which took a long time to clear, leaving a dark-colored substance floating on the surface of the Schiff

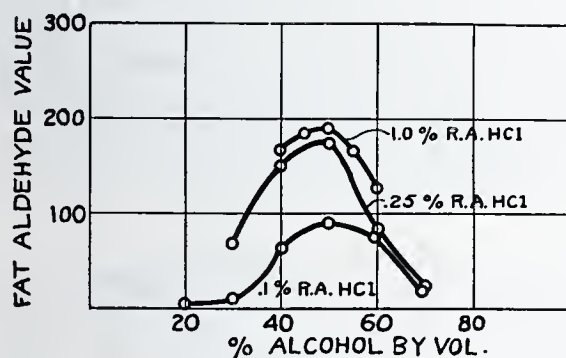


FIGURE 3. EFFECT OF ALCOHOL CONCENTRATION

reagent. This substance undoubtedly was an addition product formed by an aldehyde of high molecular weight and the Schiff reagent. It was insoluble both in the aqueous layer and the petroleum ether layer. The addition of ethyl alcohol from 30 to 50 per cent by volume entirely eliminated it, and the color intensity of the petroleum ether layer was enormously increased. The explanation of this effect is probably that the alcohol causes a dehydration of the rosaniline hydrochloride resulting in an increased solubility of the reaction product in petroleum ether.

The addition of alcohol, however, changed the color of the Schiff reagent from yellow to red, particularly when the sulfurous acid concentration was reduced far below the quantity required for the ordinary Schiff reagent. This red coloration of the yellow Schiff reagent might possibly have been caused by the presence of aldehyde impurities in the alcohol, but the same intensity of red color was also developed when carefully purified alcohol was added to the yellow Schiff reagent. Apparently the color must be due to the dehydrating effect of the alcohol, which causes the reappearance of the quinoid form of the rosaniline hydrochloride with its characteristic red color. The addition of alcohol entirely changes the character of this reagent so that it can no longer be called "Schiff reagent." The new red alcoholic reagent can be used only as a test for aldehydes readily soluble in petroleum ether.

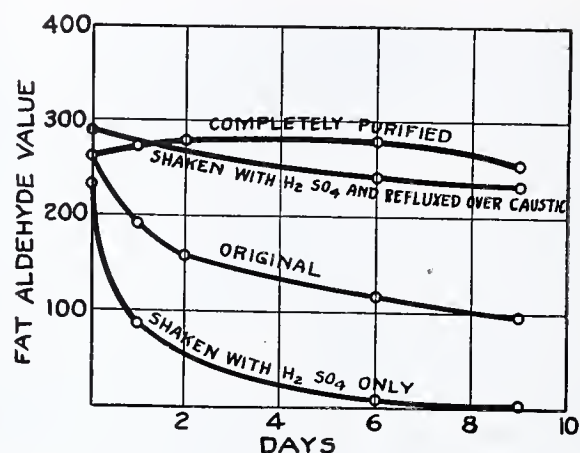


FIGURE 2. EFFECT OF IMPURITIES IN PETROLEUM ETHER

A number of factors such as the concentrations of sulfur dioxide, alcohol, and rosaniline hydrochloride were found to influence the color intensity of the petroleum ether layer when using the new reagent. A series of tests was therefore undertaken to study these various factors, and to determine the best composition of the new reagent giving the optimum color intensity and the conditions under which optimum and reproducible values are obtained.

In preparing the usual Schiff reagent it is ordinarily recommended that fuchsin in amounts of 1 to 5 grams per liter be used. After comparing several commercial grades of fuchsin it was decided to use rosaniline hydrochloride. This compound is considered to be the main constituent of the ordinary fuchsin. It crystallizes with 4 molecules of water (17.57 per cent). The commercial product, however, contains only about 9 per cent of water. Hereafter rosaniline hydrochloride is referred to in several places as R. A. HCl.

In making up the usual yellow Schiff reagent, it was found possible to reduce the prescribed amount of hydrochloric acid, thus markedly increasing the color reaction. When the reduction was carried too far, the fuchsin precipitated. When 50 per cent alcohol was added, the acidity could be decreased further without causing precipitation of the fuchsin. On standing, a crystalline precipitate, due to the presence of sodium salts, formed, but, by using an aqueous solution

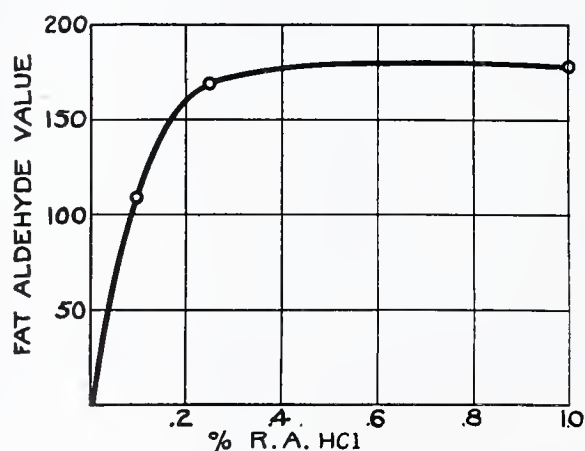


FIGURE 4. EFFECT OF R. A. HCl CONCENTRATION

of sulfur dioxide, the sodium salts were eliminated. A very marked optimum color value was obtained with 0.45 mole SO₂ per mole rosaniline hydrochloride when using a 1 per cent solution and 50 per cent alcohol by volume, as shown in Figure 1.

Petroleum ether of commercially purified grades has a tendency, on standing, to reduce the aldehyde content of a tallowy fat solution, undoubtedly owing to the presence of certain unsaturated hydrocarbons which react with the fat

aldehydes. Figure 2 shows this effect and also the effect of various methods of purification.

Figure 3 shows the effect of alcohol content on the color value. Fifty per cent alcohol by volume gave the optimum color intensity for all three concentrations of rosaniline. In making up the reagent as described below, the alcohol content will be slightly below 50 per cent by volume but, as the curve is rather flat at this point, this should have very little effect.

The relationship of concentration of rosaniline hydrochloride to color value is shown in Figure 4. One per cent was adopted as most suitable.

By varying the fat concentration, it was found that the fat aldehyde value decreases with decreasing fat concentrations, or decreasing color value. When using a 1 per cent rosaniline reagent, the fat aldehyde value reaches a maximum at a color value of about 600, after which it remains constant.

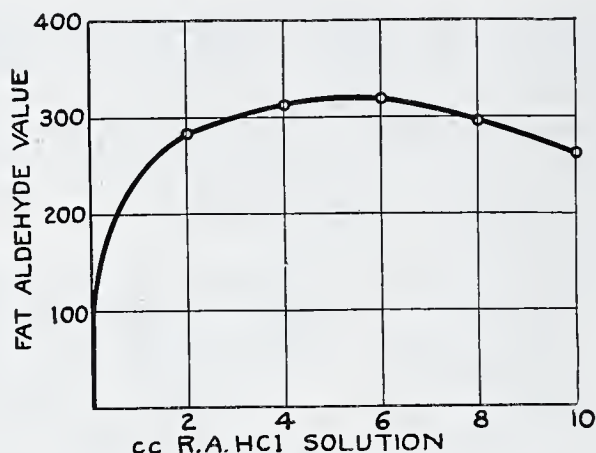


FIGURE 5. EFFECT OF VARIATION IN AMOUNT OF REAGENT USED

Several types of containers were tried out. The results varied widely, the highest values being obtained with test tubes. These should be large enough to allow room for mixing and preferably should measure 22 by 175 mm.

The manner of shaking was studied and it was discovered that a gentle rotation at a rate of 30 r. p. m. gives a much higher color than a vigorous shaking. Rotation is accomplished by placing the test tubes in a basket in such a way that when the basket is fastened to a vertically rotating disk the tubes are inverted as the disk rotates. The time of rotation giving the optimum color value was found to be 4 minutes.

The proportion of rosaniline reagent to the fat solution is also important. Five cubic centimeters of the rosaniline reagent with 25 cc. of fat solution were found convenient and gave the maximum color value, as shown by Figure 5.

If the colored petroleum ether solution is allowed to stand in contact with the rosaniline reagent after rotating, the color intensity will increase about 10 per cent during the first 3 hours and then remain constant for several hours. As the kind of glass used and the condition of its surface affect the color value on standing, it is recommended that the major part of the colored petroleum ether be pipetted into clean test tubes soon after rotating. Under these circumstances, the color value will drop slightly during the first hour, but then remain practically constant for several hours. This procedure, although it results in a lowering of the color intensity, was adopted solely for the purpose of obtaining uniformity.

Temperature has some effect on the color value. From 5° to 25° C. it is practically constant, but drops about 15 per cent at 37° C. It is therefore advisable to avoid such high temperatures.

It is recommended that the rosaniline reagent be kept in a brown bottle, since light, particularly direct sunlight, is found to be detrimental. As oxygen slowly oxidizes the sulfur dioxide, it is advisable to exclude oxygen from the bottle

holding the reagent, or to divide the freshly made reagent into several small bottles which should be completely filled and well stoppered.

PREPARATION OF REAGENT AND COLOR STANDARD. Twenty grams of pure rosaniline hydrochloride on the anhydrous basis are placed in a 1000-cc. volumetric flask with about 600 cc. of absolute alcohol. The flask is then shaken vigorously until all is dissolved, after which the flask is filled to the mark with absolute alcohol. The solution is now allowed to stand for several days during which a dark-colored sediment forms, consisting of organic impurities and nearly all of the salt. Five hundred cubic centimeters of the clear, filtered, 2 per cent solution are pipetted into a 1000-cc. volumetric flask to which are then added 133 cc. of 0.1 *M* aqueous solution of SO₂ (6.4 grams of SO₂ per liter) or its equivalent and distilled water to the mark after cooling to room temperature. The strength of the SO₂ solution is best determined by adding 0.1 *N* iodine in excess and titrating the excess back with 0.1 *N* thiosulfate.

A 0.001 per cent cresol red solution buffered to a pH value of 8.3 was used as a color standard. The buffer solution was made up as follows:

	Grams
Sodium borate (decahydrate).....	7.5477
Boric acid.....	7.5044
Sodium chloride.....	1.7696

These were dissolved in distilled water and made up in a volumetric flask to 1 liter.

One-tenth gram of cresol red on the anhydrous basis was weighed into a 100-cc. volumetric flask and dissolved in the above buffer solution and the flask finally filled to the mark with the same. From this solution 5 cc. were pipetted accurately into a 500-cc. volumetric flask and the buffer solution added up to the mark. This standard color solution matches fairly closely the shade of the fat aldehyde rosaniline color.

Both the rosaniline hydrochloride and the cresol red used were the National Medicinal Products.

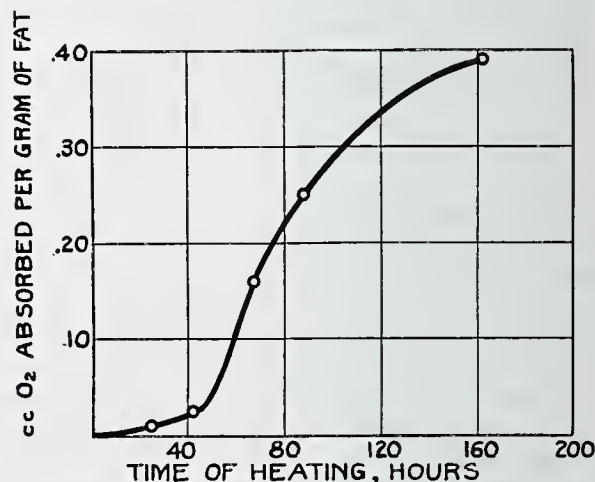


FIGURE 6. PROGRESS OF OXIDATION OF BUTTER FAT AT 50° C.

Several grades of petroleum ether were tried and, of these, the most satisfactory was Eimer & Amend's Benzine (Petroleum) Purified, b. p. 30° to 100° C. It is necessary to purify it further by shaking four or five times with concentrated sulfuric acid, 250 cc. per 2 liters of petroleum ether. The acid should be only faintly yellow after the last shaking. After that the petroleum ether is refluxed over 100 cc. of a 50 per cent caustic solution for 2 hours and finally distilled over 100 grams of calcium oxide. The higher fraction, boiling between 50° and 100° C., is collected separately to be used for the aldehyde test.

DETAILS OF TEST. The fat or oil is dissolved in purified petroleum ether to a suitable concentration varying from 0.05 to 10 grams per 100 cc. of solution, depending on the aldehyde

content. The color value, after rotating with the rosaniline reagent, should preferably be between 50 and 200. If the first test does not come within this range the test should be repeated, using a greater or less amount of the fat to bring the color value within the above range. If the solution is not quite clear, it should be filtered before making up to volume. Twenty-five cubic centimeters of the clear fat solution are pipetted into a test tube (22 by 175 mm.), and 5 cc. of the rosaniline reagent are then added with a pipet and the test tube closed firmly with a No. 4 rubber stopper covered with tin foil. The test tube is then rotated as described above for 4 minutes and, after standing for a short time, about 20 cc. of the purple petroleum ether are pipetted into a clean test tube which may be closed with the same rubber stopper covered with tin foil. A colorimetric measurement is made after standing for 1 to 2 hours, using the cresol red color standard with an arbitrary color value taken as 100. The color value of the test solution is thus measured in terms of arbitrary color units. The aldehyde content of fat is expressed in these color units on the basis of a 0.1 per cent fat solution, and these specific color units are called "fat aldehyde values."

The fat aldehyde value is calculated according to the following formula:

$$A = \frac{100 \times R_s \times 0.1}{R_t \times P}$$

where A = fat aldehyde value

R_s = reading of color standard in mm.

R_t = reading of test solution in mm.

P = percentage of fat or oil in test solution (grams of fat per 100 cc. of solution)

EXAMPLE:

P = 1.0 (1 gram of fat per 100 cc. of solution)

R_s = 10.0 mm.

R_t = (5.4-5.5-5.5-5.5) average, 5.48 mm.

$A = \frac{100 \times 10 \times 0.1}{5.48 \times 1} = 18.2$ (fat aldehyde value)

APPLICATIONS

Various kinds of fats and oils were tested for fat aldehyde values according to the new method as described above. It is interesting to note that invariably the older samples gave a higher value than the fresh ones. All these samples of fats and oils gave practically an identical color shade with the new reagent, indicating that the aldehydes formed in various fats and oils are quite alike in respect to this reaction.

TABLE I. RESULTS OF TESTS ON VARIOUS FATS AND OILS

SAMPLE	ORGANOLEPTIC TEST	FAT ALDEHYDE VALUE
Coconut oil	Good	1.7
Palm oil	Good	1.4
Whale oil	Fishy	9.5
Cod-liver oil	Relatively good	5.1
Peanut oil	Somewhat rancid	46.5
Soy bean oil	Somewhat rancid	28.0
Linseed oil	Bitter	2.6
Cocoa butter, fresh	Good	1.8
Cocoa butter, old	Good	4.7
Olive oil, fresh	Good	14.3
Olive oil, old	Rancid	71
Cottonseed oil, fresh	Good	20.0
Cottonseed oil, old	Rancid	132
Corn oil, fresh	Good	5.5
Corn oil, old	Rancid	104
Butter oil, fresh	Good	0.5
Butter oil, exposed to air	Tallowy	10.3
Suet, fresh	Good	5.0
Suet, old	Tallowy	360

OXIDATION TESTS

Ten-gram samples of pure butter fat with an original aldehyde value of 1.5 were heated in glass-sealed Pyrex flasks which contained about 126 cc. of air, or about 26 cc. of oxygen. The flasks were rotated at 50° C. for various lengths of time and the volume of absorbed oxygen calculated from data compiled regarding temperature and pressure before and after heating. The fat aldehyde values of these more or less

oxidized butter-fat samples were determined as described above. In Figure 6 are plotted the cubic centimeters of oxygen absorbed per gram of fat against time of heating. Figure 7 shows the correlation between oxygen absorption and the fat aldehyde value.

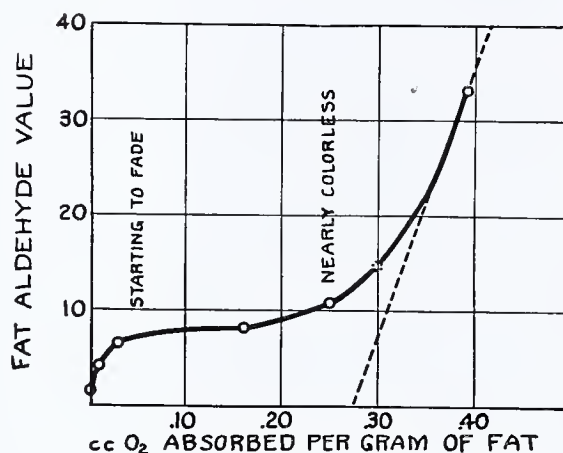


FIGURE 7. CORRELATION BETWEEN OXYGEN ABSORPTION AND FAT ALDEHYDE VALUE OF BUTTER FAT AT 50° C.

The following calculations are an attempt to correlate the oxygen absorption or the equivalent theoretical aldehyde formation with the fat aldehyde value as determined by the new method.

It is assumed that the color intensity of the rosaniline hydrochloride, when combined with a fatty glyceride aldehyde through the SO_2 linkage and dissolved in petroleum ether, is not materially different from that of the equivalent rosaniline hydrochloride dissolved in absolute alcohol.

24,000 cc. O_2 (20° C.) \approx 1 mole fat aldehyde
 \approx 1 mole rosaniline hydrochloride (R. A. HCl)
 \approx 338 grams R. A. HCl
 1 cc. $\text{O}_2 \approx$ 0.0141 gram R. A. HCl

Color value of alcoholic rosaniline hydrochloride solution:
 0.00046% R. A. HCl \approx 109 color units (color standard = 100)
 0.000422% R. A. HCl \approx 100 color units

By comparing 1 liter of rosaniline hydrochloride solution with 1 liter of a 0.1 per cent fat solution containing 1 gram of fat, the following relationship is found:

1 liter of 0.000422% R. A. HCl with color value of 100 contains 0.00422 gram of R. A. HCl

$1 \frac{0.0042}{0.014} = 0.30$ cc. of oxygen \approx 100 color units

1 cc. of oxygen per gram fat \approx 333 color units

From the curve in Figure 7 are taken the following figures:

TOTAL RANGE OF OXIDATION OBSERVED:

1 gram butter fat absorbed 0.39 cc. O_2 , acquiring a fat aldehyde value of 33.2

Increase in fat aldehyde value: $33.2 - 1.5 = 31.7$ color units

0.39 cc. $\text{O}_2 =$ theoretically $333 \times 0.39 = 130$ color units

$\frac{31.7 \times 100}{130} = 24\%$ of theoretical value

By making a similar calculation for different sections of the curve in Figure 7, values in Table II are obtained.

TABLE II. OXYGEN-FAT ALDEHYDE CORRELATION

O_2 ABSORBED PER GRAM OF FAT Cc.	INCREASE IN FAT ALDEHYDE VALUE	THEORETICAL COLOR VALUE EQUIV. TO O_2 ABSORPTION	% OF THEORETICAL COLOR VALUE	RANGE OF OXIDATION
0.39	31.7	130	24	Total
0.03	5.0	10	50	Beginning
0.22	4.3	73	6	Middle
0.14	22.4	47	48	Last part
(0.113)	(33.2)	(38)	87	End (tangent)

The low value for aldehyde formation during the middle part of the oxidation is quite significant in that it shows that during this period of decolorization of butter fat the major part of the oxygen absorbed is probably used up by the carotin contained in the butter fat, and relatively little aldehyde is formed.

A lower color value than is expected theoretically could also result from a reaction between the fat aldehyde and free sulfurous acid, which undoubtedly is present in the rosaniline reagent through dissociation of the rosaniline sulfite.

Further tests with more oxygen absorption might possibly give results which would agree even better with the theoretical values.

In order to prove that extreme oxidation of fats can result in low fat aldehyde values, a series of samples of butter fat was exposed to air at 100° C. for varying lengths of time. The results, which are given in Table III, show that the fat aldehyde value reaches a maximum of about 950 in 15 hours, after which it drops rapidly and then more slowly to below 50 at the end of 35 hours. The oxygen absorption seems to slow down after 20 hours' exposure. It is therefore probable that the reduction in fat aldehyde value during the last hours of heating is due mainly to formation of condensation products rather than to further oxidation of the aldehydes. An old sample of corn oil, which had been exposed to air at room temperature for about 6 years, gave a fat aldehyde value as low as 0.1. This sample was exceedingly off flavor. The absence of aldehydes is undoubtedly due to condensation. A similar case was found in the surface butter fat of a very old sample of whole milk powder, which had been exposed to air for 7 years.

TABLE III. OXIDATION OF BUTTER FAT AT 100° C.

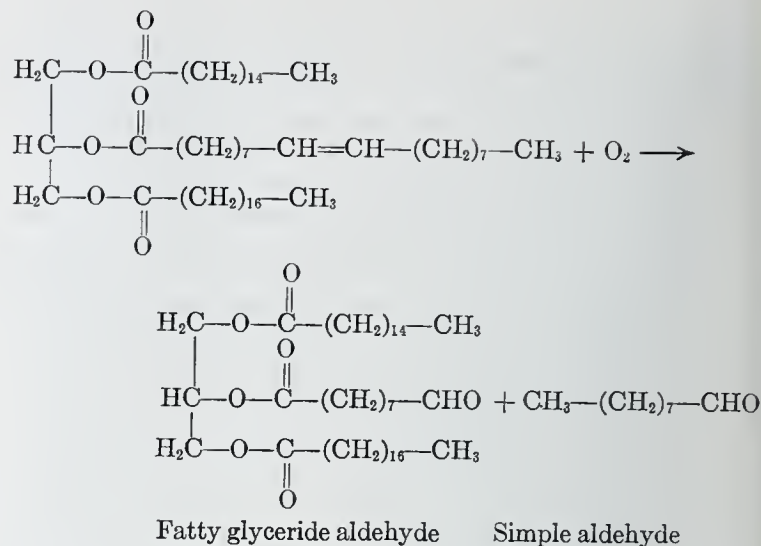
DURATION OF HEATING Hr.	O ₂ ABSORBED PER GRAM OF BUTTER FAT Cc.	FAT ALDEHYDE VALUE	REMARKS
0	0	1.2	
5	14	740	
10	20	890	
15	30	965	Maximum
20	38	257	
25	..	258	
30	40	106	
35	..	38	

DISCUSSION

Several simple aldehydes, such as butyraldehyde, heptaldehyde, cinnamaldehyde, and vanillin, do not develop any color in the petroleum ether layer when rotated with the new rosaniline reagent. Neither did samples of oleic and linoleic acid, which had quite a tallowy odor. All of these products, however, gave more or less of a color reaction with the yellow Schiff reagent. The solubility of the yellow compound decreased with increasing molecular weight. This indicated that the aldehydes which produce the color in the petroleum ether when tested with the new rosaniline reagent must have a high molecular weight, and an affinity for petroleum ether sufficient to overcome the adverse effect of the attached rosaniline group. It is reasonable to assume that these aldehydes are glyceride aldehydes formed when unsaturated acid radicals of fats are oxidized. If the oxidation proceeds according to the reaction formula which follows, then there should be formed also at the same time a simple aldehyde of low molecular weight, such as nonylaldehyde.

This reaction may possibly go through an intermediate peroxide stage, as suggested by several workers.

When tested with the usual yellow Schiff reagent, a tallowy butter fat develops relatively little of the water-soluble color which is caused by simple aldehydes. It has been shown (Figure 2) that the high acidity in the yellow Schiff reagent greatly depressed the color reaction. It is likely that the intense odor of tallowy butter fat is due to the presence of low-boiling simple aldehydes.



The coloring of the yellow Schiff reagent by aldehydes depends, according to Wieland and Schening (8), on an overbalancing of the rosaniline molecule when two molecules of aldehyde are linked to one rosaniline molecule, with the result that the leuco form is changed to the quinoid form with loss of SO₂. The reaction with a fat aldehyde probably combines in molecular proportion through the amino-sulfurous linkage with the rosaniline hydrochloride. This is already present in the colored quinoid form which apparently is preserved in the reaction product. The color shade of the reaction product is somewhat changed to a grayish purple as compared with the pure purple color of the rosaniline reagent. It is very likely that other basic dyes would react in a similar manner.

Table IV gives a comparison between the various reagents for fat aldehydes, and shows that the new improved reagent is over twenty times as sensitive as any of the other reagents.

In extraction of fats from various food products, difficulties are sometimes encountered in obtaining the total fat aldehydes present. This problem will be discussed in a later paper.

TABLE IV. COMPARISON OF VARIOUS REAGENTS FOR FAT ALDEHYDES

REAGENT	SO ₂			COLOR	RELA- TIVE COLOR IN- TENSITY	REMARKS
	FUCH- SINE OR R. A. HCl	MOLE FUCH- SINE OR R. A. HCl	FREE HCl PER MOLE FUCHSINE	VALUE		
				WITH		
				0.1% TALLOWY BUTTER FAT SOLN.		
%	<i>Mole</i>	<i>Mole</i>				
Improved rosani- line reagent	1.0	0.45	0	213	100	Purple- red
Swiss Schiff re- agent, von Fellen- berg	0.5	3.2	0.35	10.6	5.6	Yellow- orange
Russian Schiff re- agent, Inichof and Schoschine	0.1	18.2	22.0	7.3	3.4	Yellow- orange
Kreis reagent, Kerr	10.5	4.9	Orange

ACKNOWLEDGMENT

The author wishes to thank Miss W. H. van Wieren for making numerous colorimetric measurements and for offering valuable suggestions.

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RECEIVED April 15, 1931. Presented before the Division of Agriculture and Food Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

Automatic Open Cleveland Flash and Fire Equipment

Testing Laboratory, Port Arthur Works, The Texas Company

A UNIQUE and efficient improvement of the Cleveland open-cup flash tester has recently been installed in this laboratory. The apparatus is termed automatic because the application of the test flame is made in a mechanical manner which eliminates one of the personal equations heretofore regarded as a cause for discrepancy between tests as conducted by more than one operator. All requirements of the American Society for Testing Materials are met in that the standard cups, thermometers, brass plates, and asbestos boards specified in the standard procedure are used.

The unique features of this tester, aside from the mechanical application of the test flame, include the use of sensitive valves by which the heating rate can be more accurately maintained, the solid circular shield around the cups which prevents air circulation in the area between the cups and thus eliminates constant relighting of the test flame, the special thermometer supports, the small pilot lights for lighting both the gas flame and the test flame, and the exhaust system by which most of the hot gases are removed from the testing room, always a source of discomfort to the operator under the best operating conditions.

Another feature considered for making this test more mechanical has been the application of the testing medium by means of a spark gap rather than by gas, but this has not yet been developed satisfactorily. Some time has been spent on the development of a constant-level cup to take care of the expansion within the cup when high-flash oils are being tested, but this also has not been successfully accomplished as yet. Reference to the figure will make the description clearer. Aside from complying with all the A. S. T. M. requirements, this machine eliminates at least four variables which are present when the test is carried out manually: (1) The test flame is moved exactly in a plane parallel with the top of the cup; (2) a uniform rate of exactly 2.5 inches (6.35 cm.) per second is maintained; (3) the thermometer is immersed exactly the same depth for each test because of a positive stop; and (4) the test flame approaches more nearly to the size of that specified than those in common use.

The machine has a capacity of five cups, *C*, each resting on a standard brass plate, *BP*, and surrounded with a standard asbestos plate, *AP*. A hood, *A*, covers all flames and is lined in the top with asbestos board.

Between the burners, *I*, are flues, *F*, which are connected with an exhaust system to carry off the

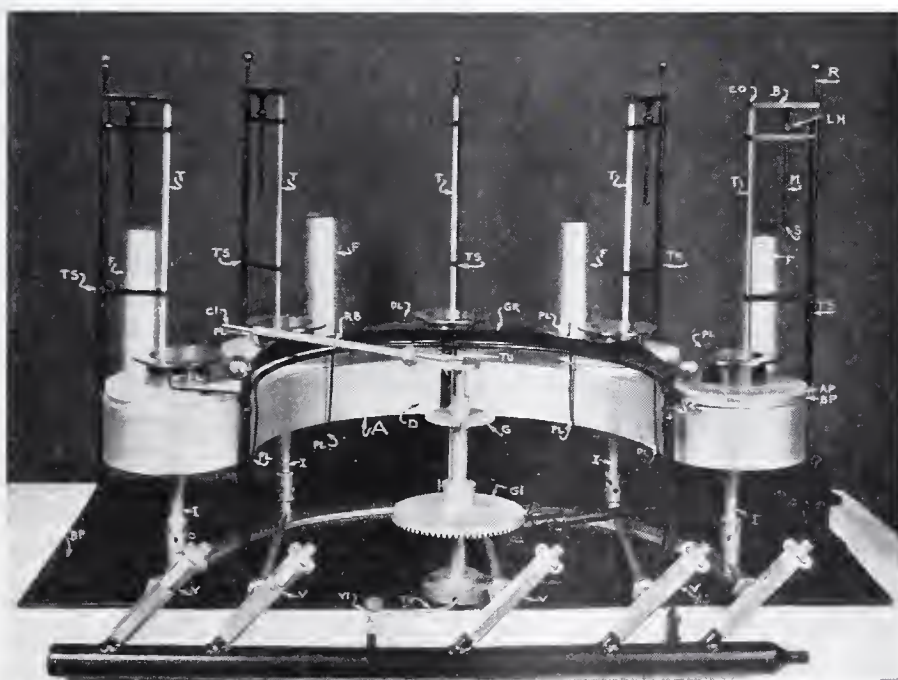
gases and excess heat. The cups are placed on an arc through which the revolving test-flame burner, *RB*, moves, with the test-flame tip, *Cl*, passing directly over the center of the cups.

Four risers are placed on the guide rail, *GR*, so that the test burner will rise and stop between each successive cup. The test burner is hinged on a pedestal and moves forward by arm *D* engaging in gear *G*. As *RB* moves up on the elevations, arm *D* disengages with gear *G*, and the burner stops. The operator is then free to continue the movement of the test flame to that particular flash cup, or to move the flame to any desired cup for testing. The test flame is revolved by a motor through a reduction gear, *G1*, and a set of bevel gears. The speed of the burner tip is 2.5 inches (6.35 cm.) per second, as specified in the standard method.

Another feature of this machine is the means used for placing the test flame on the cup. To make the test flame start across the cup each time and not hang onto the edge, a slope is provided on the riser and so placed that the test flame will start about midway on the flange of the cup. The heating burners are arranged on an arc directly under each cup, and each burner is controlled by a sensitive valve, *V*. This feature alone is a big improvement, and gives the operator complete control of the heat, as it requires several turns of the valve stem to change the heat a great deal. The test flame is controlled by valve *VI* through rubber tubing, *TU*, which goes up through the pedestal to *TU* and onto copper tubing. The pilot lights, *PL*, are controlled by valve *V2*, there being one light over each burner and one just at the edge of each flash cup.

The thermometers, *T*, are held in a sliding frame, *TS*. A rod, *R*, which is welded to an arm, *B*, slides up and down in *TS*. A bolt, *N*, passes through a guide arm welded onto *TS*, screws into arm *B*, and is held tight by a lock nut. Two lock nuts, *LN*, on this bolt form an adjustable stop for the thermometers, allowing an initial adjustment which will remain permanent. The head of the bolt, *S*, forms an upward stop to protect the thermometer from breakage.

The thermometer itself is supported by an arrangement consisting of a pin, *CO*, which runs through the eye on top of the thermometer, and is lowered into a round recess. The pin is slightly longer than the diameter of the thermometer. The recess is covered with a slide which retains the thermometer in place, and also allows the free rotation of the thermometer for easy reading.



FLASH AND FIRE TEST MACHINE

RECEIVED December 9, 1931.

Total Solids in Natural Brines

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MANY workers omit determination of total solids in brines because it is obviously a difficult determination of questionable reliability. It is rather obvious, for instance, that the heat applied is likely to decompose some salts present or fail to dehydrate them. Sweeney and Withrow (5) state that "brines rich in calcium chloride require a rather high temperature, above 160° C., to expel the water completely. At this temperature magnesium and calcium salts lose a part of their acid constituents," whereas Efremov holds (1) that "direct evaporation is likely to cause trouble owing to hydrolysis and hygroscopicity. Add 2.0 to 2.5 times as much anhydrous Na_2CO_3 dissolved in hot water, evaporate to dryness, heat at 105° C. for one hour and then at 150° C. for 5 to 6 hours."

Phalen, who appears to have done the most work on brines (4), reports that for total dissolved salts "a convenient volume of the dilute solution was evaporated to dryness in a weighed platinum dish and the residue was heated to constant weight at 105° C., cooled, and weighed. This estimate is not reported but was used as a check on the analysis." Mellor in his discussions of properties of magnesium chloride (2) states that "the hydrated salt cannot be dehydrated without a loss of hydrogen chloride by simple heating, that according to F. P. Dunnington and F. W. Smither, all but one mole of the water of crystallization can be expelled at 98° without decomposition, and the principal loss of hydrogen chloride occurs during the expulsion of the residual water." Mellor further states (3) regarding properties of calcium chloride that according to Bunsen, "even after the salt has been melted at a white heat, it retains enough water to develop hydrogen when melted with iron," and according to A. Weber, "the salt dehydrated at 200° C. is anhydrous."

The literature is conflicting regarding decomposition of magnesium and calcium chlorides. Numerous temperatures (98° to 157° C.) are reported at which magnesium chloride hexahydrate begins to decompose.

In any event we should have more precise information, since the value of this determination cannot be neglected as it serves the double purpose first of giving the engineer (manufacturer) figures which could be used in calculating fuel requirements for evaporation, and second, of serving as a check on the analysis. Therefore, in this investigation pure salts (c. p.) corresponding to the major constituents of the total solids in natural brines, such as sodium, calcium, and magnesium chlorides, were used.

First, the salts in solution were subjected to heating at various temperatures separately, then mixtures of these solutions were also subjected to the same heating conditions to learn precisely what their behavior was under the customary

Ignition at 750° C. appears to be the most reliable method for determining total solids in natural brines containing mixtures of magnesium, calcium, and sodium chlorides as major constituents, as well as being most certain as to composition of final ignited residue. Necessary corrections must be made according to the formula proposed in this paper.

Although heating a 25-cc. portion of the natural brine to constant weight at 150° C. gives fairly satisfactory results, the time required to reach constant weight and the necessary breaking up of the residue to ensure maximum evaporation of the enclosed water makes this determination too tedious and subject to errors.

Since magnesium chloride solutions have a tendency to decompose at low temperatures (above 95° C.) results obtainable by heating mixtures of the various pure salts to constant weight at 150° C. were not sufficiently reliable. Results at 105° and 120° C. were sometimes as much as 12 per cent in error.

total solids determination conditions.

This work indicated:

1. Ignition to constant weight at 750° C. was the most satisfactory, quickest, and most reliable method for total solids determination.

2. Low temperatures such as 100° to 150° C. required considerable time for evaporation, and the accuracy of the results varied largely depending on the relative amounts of the constituents.

3. Magnesium chloride hexahydrate decomposed practically at all temperatures above 95° C. (much below the temperature of complete dehydration) the rate and extent of decomposition depending upon the temperature and length of heating.

4. Magnesium chloride did not lose all its chlorine at 750° C., as analysis of the ignited residue indicated the presence of some residual chlorine.

5. Calcium chloride apparently does not readily dehydrate, retaining 2 to 3 per cent water after being subjected to heating at 150° C. for 40 to 50 hours. It decomposed only slightly at

750° C. (less than 0.5 per cent).

6. Sodium chloride dry or in solution does not show loss due to decomposition or volatilization when dried at 750° C. in a muffle furnace.

7. Mixed solutions of these salts show greater loss due to volatilization and decomposition when ignited at 750° C. than do the salts alone.

EXPERIMENTAL PROCEDURE

SOLUTIONS. Stock solutions of the pure salts of magnesium chloride (hexahydrate), anhydrous calcium chloride, and sodium chloride, c. p., were prepared by weighing 20 grams of each salt and dissolving each in 500 cc. of distilled water.

SAMPLES. Different concentrations of these solutions were subjected to the same heating conditions to see if dilution of the solution would have any effect on the final result.

ANALYSIS. Twenty-five cubic centimeters of each of these stock solutions were diluted to 1000 cc., and 25 cc. of these diluted solutions were then used for titrating with 0.1 *N* silver nitrate solution using potassium chromate indicator (chlorine-free). The chlorine content of each solution was used as a basis in calculating the purity of the salts. Filtration of the calcium chloride solution was found to be necessary, as a certain amount of insoluble matter remained in the solution when preparing stock solution.

HEATING. Three different samples were used for each concentration or mixture of the salts, marked 1, 2, 3. Sample 1 was ignited at 750° C. to constant weight after an initial drying at 105° C. to prevent loss by spattering. Sample 2 was placed in an oven at 105° C. and heated to constant weight, and sample 3 was dried at 120° C. to constant weight, cooled, and weighed. Samples 2 and 3 were then both placed in an oven at 150° C., allowed to reach constant weight, again cooled and weighed, and finally ignited at 750° C. in a muffle furnace.

This stepwise drying of samples 2 and 3 was for comparison with direct ignition on the rate and extent of decomposition.

STABILITY OF VARIOUS SALT SOLUTIONS UNDER HEATING CONDITIONS

Tables I through V show the study of the behavior of salt solutions under heating conditions. Because of limited space, data on several of the systems studied, such as pure calcium chloride and pure sodium chloride, have been omitted.

MAGNESIUM CHLORIDE. The data of Table I show distinctly that all solutions of magnesium chloride, regardless of concentration, decompose, the extent of decomposition depending upon the temperature and length of heating.

Assuming, however, that magnesium chloride solutions dehydrate without decomposition and calculate as such, the recovery at 105° C. (100 per cent concentration) is 131.6 per cent (column C), the recovery at 120° is 124.9, at 150°, 103.1, and at 750° C. only 43.5 per cent. The recovery as per cent of original sample at 150° C. at this concentration appears to be the best, but not at all concordant, as indicated by the results and per cent error at different concentrations. The results obtained at 750° C. (calculated as magnesium chloride) were very consistent, with the sole exception of 2.5 per cent concentration, which was 42.8 per cent. These 750° C. results were closer to the facts as shown by both recovery and per cent error, and conclusively prove the instability of magnesium chloride at this temperature.

Analysis of the residues at 150° and 750° C. showed that loss of chlorine was greatest at 750° C., where there was a chlorine content of approximately 0.005 gram, present probably as MgOCl₂ or MgO.MgCl₂.

Since the loss of chlorine appeared obvious at the temperatures employed and reached a maximum decomposition at 750° C., the original weight of the sample was calculated (column D) as magnesium oxide instead of magnesium chloride (column B). When the weight of the dry residue was divided by the weight of the original sample, it gave as per cent recovered 102.6 per cent at 750° C. The results at all the other temperatures should of course give correspondingly higher values with this method of calculation.

The column marked "Error" gave excellent support to the conclusions in that the variations in per cent error were much greater for 150° than they were for 750° C. In the latter case the error was small and not affected by concentration or duration of evaporation.

The final conclusion was that magnesium chloride solutions did not dehydrate uniformly at low temperatures. A temperature of at least 700° C. should be employed for more uniform results. High dilutions appeared to be the severest test for studying evaporation conditions and influence. Therefore, dilute solutions were used in all subsequent work.

MAGNESIUM AND CALCIUM CHLORIDES. The data of Table II show that with increase in temperature of drying for any concentration of magnesium and calcium chlorides, there was a corresponding decrease in per cent recovery approaching the true value at 150° C. only. However, as the concentration of magnesium chloride decreased in the mixture, the per cent recovered at 750° C. rose from 72.5 to 96.2. This was calculated under the assumption that magnesium chloride did not decompose at 750° C. If calculated on the basis of 100 per cent decomposition into MgO, then the per cent recovered as of original weight of sample (column E) was

TABLE I. MAGNESIUM CHLORIDE (HEXAHYDRATE) SYSTEM

CONCENTRA- TION OF MgCl ₂	TEMP. OF DRYING ° C.	WT. AFTER DRYING			TOTAL SOLIDS				E. MgO recovered %	ERROR	
		1	2	3	A. Residue av.	B. Original sample	C. Residue in original	D. Original sample as MgO		$\frac{B - A_{150^\circ}}{B} \times 100$	$\frac{D - A_{750^\circ}}{D} \times 100$
		Gram	Grams	Grams	Grams	Grams	%	Gram		%	%
100 (solid)	105		1.541		1.541	1.1711	131.6	0.496			
	120				1.461	1.1711	124.9	0.496			
	150		1.23	1.184	1.207	1.1711	103.1	0.496			
	750	0.509	0.509	0.509	0.509	1.1711	43.5	0.496	102.5	- 3.8	-2.6
50	105		1.498		1.498	1.1711	128.2	0.496			
	120			1.416	1.416	1.1711	120.5	0.496			
	150		1.22	1.104	1.165	1.1711	99.6	0.496		5.7	
	750	0.502	0.513	0.509	0.508	1.1711	43.4	0.496	102.5		-2.4
25	105		1.504		1.504	1.1711	128.7	0.496			
	120			1.439	1.439	1.1711	123.0	0.496			
	150		1.343	1.123	1.233	1.1711	105.2	0.496		- 5.3	
	750	0.507	0.509	0.510	0.508	1.1711	43.4	0.496	102.5		-2.4
10	105		1.558		1.558	1.1711	133.1	0.496			
	120			1.471	1.471	1.1711	125.7	0.496			
	150		1.48	1.126	1.301	1.1711	111.2	0.496		-11.1	
	750	0.512	0.509	0.510	0.510	1.1711	43.6	0.496	102.9		-2.8
2.5	105		1.521		1.521	1.1711	129.9	0.496			
	120			1.460	1.460	1.1711	124.3	0.496			
	150		1.334		1.334	1.1711	114.0	0.496		-13.7	
	750	0.500	0.508	0.490	0.502	1.1711	42.8	0.496	101.1		-1.2

TABLE II. MAGNESIUM CHLORIDE-CALCIUM CHLORIDE SYSTEM

SALT IN 25 CC. OF SOLN.		TEMP. OF DRYING ° C.	WT. AFTER DRYING			TOTAL SOLIDS					ERROR	
MgCl ₂	CaCl ₂		1	2	3	A. Resi- due av.	B. Ori- ginal sample	C. Resi- due in original	D. Ori- ginal sample as MgO + CaCl ₂	E. Re- covery	$\frac{B - A_{150}^{\circ}}{B} \times 100$	$\frac{D - A_{750}^{\circ}}{D} \times 100$
Gram	Grams		Grams	Grams	Grams	Grams	Grams	%	Grams	%	%	%
0.264 (50%)	0.473 (50%)	105		0.928		0.928	0.737	126.1	0.585			
		120			0.923	0.923	0.737	125.3	0.585			
		150		0.757	0.746	0.751	0.737	101.9	0.585			
		750	0.527	0.544	0.533	0.534	0.737	72.5	0.585	91.2	-1.9	8.7
0.211 (25%)	1.134 (75%)	105		1.610		1.610	1.345	119.8	1.223			
		120			1.573	1.573	1.345	117.0	1.223			
		150		1.516	1.365	1.440	1.345	107.0	1.223		-7.6	
		750	1.171	1.165	1.184	1.173	1.345	87.2	1.223	96.1		4.1
0.105 (10%)	1.710 (90%)	105		1.937		1.937	1.815	106.7	1.755			
		120			1.923	1.923	1.815	106.0	1.755			
		150		1.834	1.862	1.848	1.815	101.9	1.755		-1.8	
		750	1.716	1.696	1.698	1.697	1.815	93.5	1.755	96.6		3.3
0.0529 (5%)	1.795 (95%)	105		2.015		2.015	1.847	108.9	1.812			
		120			1.825	1.825	1.847	98.8	1.812			
		150		1.874	1.827	1.850	1.847	100.1	1.812		-0.6	
		750	1.760	1.780	1.740	1.760	1.847	95.3	1.812	97.2		2.8
0.0264 (2.5%)	1.845 (97.5%)	105		2.060		2.060	1.871	111.7	1.856			
		120			1.945	1.945	1.871	104.7	1.856			
		150		1.890	1.905	1.897	1.871	102.0	1.856		-1.4	
		750	1.799	1.806	1.781	1.795	1.871	96.2	1.856	97.8		3.3

TABLE III. MAGNESIUM CHLORIDE-SODIUM CHLORIDE SYSTEM

SALT IN 25 CC. OF SOLN. MgCl ₂ NaCl		TEMP. OF DRYING ° C.	WT. AFTER DRYING			TOTAL SOLIDS				E. Re- covery %	ERROR	
			1	2	3	A. Residue av. Grams	B. Original sample Grams	C. Residue in original %	D. Original sample as MgO + NaCl Grams		$\frac{B - A_{150}^\circ}{B} \times 100$ %	$\frac{D - A_{750}^\circ}{D} \times 100$ %
0.527 (50%)	0.999 (50%)	105		1.656		1.656	1.526	108.5	1.222			
		120			1.637	1.637	1.526	107.2	1.222			
		150		1.485	1.558	1.521	1.526	99.7	1.222			
		750	1.145	1.191	1.187	1.174	1.526	77.0	1.222	96.2	0.32	3.94
0.132 (25%)	0.750 (75%)	105		0.928		0.928	0.882	105.1	0.806			
		120			0.912	0.912	0.882	103.6	0.806			
		150		0.860	0.856	0.858	0.882	97.3	0.806		2.72	
		750	0.769	0	0.801	0.785	0.882	88.3	0.806	97.4		2.6
0.053 (10%)	0.900 (90%)	105		0.975		0.975	0.953	102.4	0.922			
		120			0.972	0.972	0.953	102.1	0.922			
		150		0.941	0.946	0.943	0.953	99.0	0.922		1.05	
		750	0.899	0.910	0	0.905	0.953	95.0	0.922	98.3		1.84
0.026 (5%)	0.950 (95%)	105		0.994		0.994	0.976	101.8	0.961			
		120			0.990	0.990	0.976	101.4	0.961			
		150		0.980	0.978	0.979	0.976	100.3	0.961		-0.37	
		750	0.955	0	0.957	0.956	0.976	96.0	0.961	99.6		0.52
0.013 (2.5%)	0.975 (97.5%)	105		1.004		1.004	0.988	101.1	0.981			
		120			0.995	0.995	0.988	100.7	0.981			
		150		0.995	0.986	0.990	0.988	100.1	0.981		-0.24	
		750	0	0.985	0.975	0.980	0.988	97.9	0.981	99.8		0.12

TABLE IV. CALCIUM CHLORIDE-SODIUM CHLORIDE SYSTEM

SALT IN 25 CC. OF SOLN. CaCl ₂ NaCl		TEMP. OF DRYING ° C.	WT. AFTER DRYING			TOTAL SOLIDS				E. Re- covery %	ERROR	
			1	2	3	A. Residue av. Grams	B. Original sample Gram	C. Resi- due in original %	D. Ori- ginal sample as K ^a Grams		$\frac{B - A_{150}^\circ}{B} \times 100$ %	$\frac{D - A_{750}^\circ}{D} \times 100$ %
0.473 (50%)	0.500 (50%)	105		1.002		1.002	0.973	103.0	0.954			
		120			0.992	0.992	0.973	102.0	0.954			
		150		0.985	0.992	0.989	0.973	101.6	0.954		-1.6	
		750	0.968	0.952	0.936	0.952	0.973	98.0	0.954	99.9		0.28
0.236 (25%)	0.750 (75%)	105		1.014		1.014	0.986	102.5	0.966			
		120			1.001	1.001	0.986	101.5	0.966			
		150		1.001	0.994	0.998	0.986	101.2	0.966		-1.2	
		750	0.983	0.968	0.945	0.966	0.986	98.1	0.966	100.0		0.00
0.095 (10%)	0.900 (90%)	105		1.008		1.008	0.995	101.4	0.985			
		120			1.016	1.016	0.995	102.0	0.985			
		150		1.008	1.012	1.010	0.995	101.5	0.985		1.5	
		750	0.992	0.982	0.984	0.986	0.995	99.1	0.985	100.0		0.00
0.047 (5%)	0.950 (95%)	105		1.009		1.009	0.997	101.1	0.997			
		120			1.116	1.116	0.997	111.1	0.997			
		150		1.006	1.017	1.011	0.997	101.4	0.997		-1.4	
		750	1.003	0.984	0.995	0.994	0.997	99.7	0.997	99.7		0.30
0.024 (2.5%)	0.975 (97.5%)	750	0.998	0	0	0.998	0.999	99.9	0.999	99.9		0.0

^a K = 0.02 (when CaCl₂ content is between 25-50%)
= 0.01 (when CaCl₂ content is between 10-20%)
= 0.00 (when CaCl₂ content is less than 10%)

higher, though much below its true value. The maximum was 97.8 per cent for a mixture containing 2.5 per cent of magnesium chloride and 97.5 per cent of calcium chloride. This loss of 2.2 per cent was apparently due to volatilization of the salts. It was not determined whether or not this loss was due to volatilization of the calcium or magnesium salt or both.

It was obvious that high concentrations of magnesium chloride in the mixture had profound influence in bringing about greater decomposition and volatilization losses of calcium chloride, amounting to about 8 per cent when a 50-50 mixture of magnesium and calcium chlorides in solution was dried and heated to 750° C. This loss decreased with decreasing quantities of magnesium chloride (91.2 to 97.8 per cent recovery).

The results at 105° and 120° C. were very irregular, whereas at 150° C. practically all concentrations gave fairly concordant results close to correct values, suggesting that this temperature was apparently the best one for drying. This neglected the fact, however, that both salts lost chlorine at this low temperature (hydrochloric acid odor and also titration for total chlorides showed the loss) although, on the basis of weight of original sample and final dry residue (apparently dry), there should be no loss of chlorine, since the dry residue weighed more than the original sample—i. e., the salt alone, without the water which was added for the purposes of these investigations. The per cent error at 150° C. was too irregular for satisfactory factorial treatment.

Therefore, the final conclusion must be that, when a mixture of salts in solution is dried at low temperatures such as used in this work, there is a tendency for the salt mixture to retain a part of the water added as a hydrate, while decomposition also takes place. Since in some of the cases studied check results were obtained, this was probably due to the fact that the amount of decomposition and amount of water retained by the salts approximately balanced each other, making these results seem satisfactory to casual observation.

Even though the results at 750° C. with mixtures are low, they are reliable and consistently connected inversely with magnesium content, showing a rational basis for factorial calculation.

MAGNESIUM AND SODIUM CHLORIDES. Table III shows characteristics similar to those of Table II—namely, the behavior of mixed salt solutions differed from the behavior of individual salt solutions under the same evaporation conditions.

With this mixture both 105° and 120° C. gave high results directly proportional to the magnesium content which could be treated factorially. The 150° and 750° C. treated results are inversely proportional to the magnesium content. The per cent error at 150° C. was entirely too erratic for factorial treatment, but the error at 750° C. gave a good curve dependent upon the magnesium content.

The table shows, at high concentrations of magnesium chloride in the sodium chloride solution (50-50 mixture), a per cent recovery of 108.5 for 105°, 107.2 for 102°, 99.7 for 150°, and 77.0 per cent for 750° C., assuming that magnesium

TABLE V. MAGNESIUM CHLORIDE-CALCIUM CHLORIDE AND SODIUM CHLORIDE SYSTEM

SALT IN 25 CC. OF SOLUTION			TEMP. OF DRYING	WT. AFTER DRYING			TOTAL SOLIDS					ERROR	
MgCl ₂	CaCl ₂	NaCl		1	2	3	A. Residue av.	B. Original sample	C. Residue in original	D. Original sample as K ^a	E. Recovery	$\frac{B - A_{150}}{B} \times 100$	$\frac{D - A_{750}}{D} \times 100$
Gram	Gram	Gram	° C.	Gram	Grams	Gram	Grams	Gram	%	Gram	%	%	%
0.132 (25%)	0.236 (25%)	0.50 (50%)	105		0.991		0.991	0.868	114.1	0.788	125.8		
			120			0.909	0.909	0.868	104.7	0.788	115.1		
			150		0.885	0.880	0.883	0.868	101.9	0.788	112.0		
			750	0.788	0.793	0.782	0.788	0.868	90.8	0.788	100.0	-1.58	0.0
0.053 (10%)	0.189 (20%)	0.70 (70%)	105		0.976		0.976	0.942	103.6	0.909	107.5		
			120			0.970	0.970	0.942	103.0	0.909	106.8		
			150		0.957	0.953	0.955	0.942	101.5	0.909	105.1	-1.38	
			750	0.907	0.911	0.905	0.908	0.942	96.5	0.909	100.1		0.11
0.026 (5%)	0.142 (15%)	0.80 (80%)	105		1.013		1.013	0.968	104.2	0.952	105.0		
			120			0.989	0.989	0.968	102.1	0.952	103.9		
			150		0.987	0.983	0.985	0.968	101.8	0.952	103.4	-1.70	
			750	0.942	0	0	0.942	0.968	97.4	0.952	99.0		1.05
0.013 (2.5%)	0.095 (10%)	0.878 (87.5)	750	0.975	0	0	0.975	0.986	98.9	0.978	99.8		0.37

^a Magnesium chloride in original sample calculated as MgO; for values of K see footnote, Table IV, for CaCl₂ corrections.

chloride did not decompose. On this assumption the 150° C. gave the best results with a per cent error ranging from 2.72 to -0.37 per cent. If we assume, however, that magnesium chloride decomposed into magnesium oxide and calculate the per cent recovery at 750° C. only (because it was obvious that those at low temperatures gave untrue values), this recovery ranged between 96.2 and 99.8 per cent for a 50-50 mixture of magnesium and sodium chlorides down to 2.5 of magnesium chloride and 97.5 per cent of sodium chloride, again demonstrating that the presence of magnesium meant loss of the other chlorides.

The per cent recovery in the case of magnesium-sodium chloride mixtures, however, was higher as compared with the magnesium-calcium chloride system. The influence of high concentrations of magnesium chloride in the mixtures in bringing about decomposition of the salts which otherwise would not decompose under the same heating conditions is probably not new (no reference was found), but is of great interest and may be useful in cases where at least two such salts are involved in a mixture.

CALCIUM AND SODIUM CHLORIDES. In Table IV the results at 105° C. were high, varying directly as the calcium chloride content. Those at 120° C. were very irregular, and those at 150° C. were high and independent of the calcium chloride content though close to the facts. A factor could be used on the error. The results at 750° C., also assuming no decomposition, were low and smoothly, though inversely, proportional to the calcium chloride content.

recovery, thus indicating that the loss of 2 per cent at a 50-50 mixture was due to volatilization and not decomposition.

MAGNESIUM-CALCIUM AND SODIUM CHLORIDES. Table V represents data obtained on mixtures of all the three salts in solution. Column C, as heretofore, represents the recovery of the sample as residue after drying at various temperatures. With the assumption that magnesium chloride does not decompose, the per cent recovery at the various temperatures was high and decreased as the concentration of magnesium chloride decreased, except in the case of 150° C. when the results were not so high but were erratic. At 750° C. just the opposite takes place, in that the recovery increased from 90.8 to 98.9 per cent. It is known, and also was found, that magnesium chloride decomposes at 750° C. and that there is approximately 2 per cent loss of calcium chloride also at high concentrations of this salt in the mixture (Table IV), hence upon recalculating (magnesium chloride as magnesium oxide and using the factor indicated in the note), a recovery of 100 per cent at 750° C. (column E) was obtained as per cent residue with practically all mixtures of the three salts in solution. The column "Error" also proved this. The column for 150° C. is very tempting in the smoothness of its results. A factor should work well for calculating results, but the 750° C. is a definitive procedure so far as chemical ending is concerned.

GENERAL DISCUSSION

1. The behavior of the salt mixtures under heating conditions was different from those of the individual salts in solution.
2. Evidently the temperature used by Sweeney and Withrow gave apparently excellently concordant and correct-appearing results for some brine compositions. However, the chemical inconsistency found in these results makes this temperature inadvisable, as it inevitably will result in gross error with some brine compositions.
3. Phalen used 105° C. for determining total solids, thus neglecting completely the facts that complete dehydration of calcium chloride does not take place at 105° C. and that magnesium chloride decomposes at a temperature of 95° C., making possible errors, as shown in this work, of as high as 12 per cent. Any apparently useful results at 105° C. must have been a balancing of errors.
4. Summarizing the information gained through these investigations the following formula has been deduced for the calculation of total solids in natural brines:

$TS = R + 0.577 \times \text{MgCl}_2 + K \times \text{CaCl}_2$

where TS = total solids
R = residue (weight) at 750° C.
 $0.577 = \frac{\text{MgCl}_2 - \text{MgO}}{\text{MgCl}_2}$

TABLE VI. ANALYSIS OF TYPICAL SAMPLES OF NATURAL BRINES

(Showing application of recommended method)			
Determination.....	1	2	3
Specific gravity at 62° F.....	1.194		
Specific gravity at 88° F.....		1.225	1.218
Deposit on aëration.....	0.03	0.01	0.01
Silica, gram.....	0.01	0.04	0.01
Iron and alumina, gram.....	0.02	0.23	0.02
Calcium chloride, grams.....	9.90	11.43	11.27
Calcium sulfate, gram.....	0.05	0.03	0.07
Magnesium chloride, grams.....	2.17	1.76	3.32
Magnesium bromide, gram.....	0.17	0.09	0.21
Sodium chloride, grams.....	10.40	13.17	11.30
Potassium chloride, gram.....	0.27	0.27	0.43
Total solids (by summation), grams.....	23.02	27.03	26.64
Total solids (by calculation), grams.....	23.07	26.88	26.70
Total solids at 150° C., grams.....	23.24	27.50	26.60
Total solids at 105° C., grams.....	25.60	30.37	29.55

The results obtained by heating different concentrations of calcium and sodium chlorides in a solution show also that there was a loss of 2 per cent of residue recovery at 750° C. for a 50-50 mixture, this recovery increasing with decrease in percentage of calcium chloride in the mixture approaching the true value 100 per cent. When analyzed for total chlorides, the residues gave a figure which, when calculated back to the corresponding chlorides, resulted in a 100 per cent (practically)

$K = 0.02$ for brines containing $\text{CaCl}_2 = 25$ to 50% of sodium chloride content
 $= 0.01$ for brines containing $\text{CaCl}_2 = 10$ to 20% of sodium chloride content
 $= 0.00$ for brines containing $\text{CaCl}_2 =$ less than 10% of sodium chloride content

To illustrate the application of this formula and method of calculation, the following examples, with data taken from Table VI, column 1, are given (slide rule used for all calculations):

$$TS = R + 0.577 \times \text{MgCl}_2 + K \times \text{CaCl}_2$$

Total solids by ignition ($750^\circ \text{C}.$).....	$R = 21.62$
0.577×2.17	1.252
0.02×9.90	0.198
Total solids calculated.....	23.07
Total solids by summation of analytical data.....	23.02

Error = $\frac{23.02 - 23.07}{23.02} \times 100 =$	0.21%
Total solids at $150^\circ \text{C}.$ (assuming no decomposition) = 23.24	
Error = $\frac{23.02 - 23.24}{23.02} \times 100 =$	0.95%
Total solids at $105^\circ \text{C}.$ (assuming no decomposition) = 25.60	
Error = $\frac{23.02 - 25.60}{23.02} \times 100 =$	11.6%

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Determination of Iodine in Soils

A New Method

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SINCE iodine occurs in very minute quantities in nature, an accurate method for its determination in rocks and soils is highly desirable because no iodine survey is complete without a fairly definite knowledge of the amount of iodine contained in the rocks and soils of the region studied.

One of the principal difficulties encountered in an investigation to ascertain whether or not any region of country is adequately supplied with iodine has been the lack of a satisfactory method for the determination of the element in rocks and soils, which, after all, are the principal sources of iodine for plants and animals on land. The methods used heretofore for the determination of iodine in rocks and soils have consisted in fusing a relatively small quantity of either of these materials with potassium hydroxide or the extraction with dilute acids. The methods are tedious, cumbersome, and probably subject to considerable errors.

EXPERIMENTAL PROCEDURE

Tests made on the water extract from 100 grams of burned lime showed that no iodine was present. This fact led to the inference that the limestone from which the lime was burned either did not contain iodine or it had been volatilized

during the burning. It can be demonstrated that most limestones contain iodine, as tests for its presence can be obtained by leaching 1000 grams of finely pulverized stone with distilled water, evaporating the filtrate to dryness, extracting the residue with alcohol, evaporating the alcoholic extract to dryness, and testing this residue for iodine by the carbon disulfide method. Apparently the iodine compound is volatilized when the stone is heated intensely, and should be recoverable from the gaseous products.

Accordingly, an electric combustion-tube furnace was obtained for the purpose of burning as much as 100 grams of limestone or soil in a partially closed combustion tube and aspirating the volatile matter through a 5 per cent solution of potassium carbonate contained in a series of wash bottles.

Figure 1 shows the apparatus ready for use: 1 is an electric combustion-tube furnace having a 50-mm. hole through the center; 2, a quartz combustion tube, inside diameter 40 mm., outside diameter 50 mm.; 3, a sillimanite combustion boat, 250 by 32 by 20 mm.; 4, a rheostat; and 5, gas wash bottles containing a 5 per cent solution of potassium carbonate. Three bottles are used. The combustion tube is inserted in the hole in the furnace.

From 25 to 100 grams of soil or small pieces of rock are weighed into the combustion boat. The amount of material depends on whether the iodine content is high or low. Some limestone contains enough iodine to permit a determination to be made on 25 grams by this method. Other rather pure limestone requires 100 grams, whereas sandstone rocks require 100 grams of material, and soils 25 to 50 grams.

The small end of the quartz combustion tube is connected with three gas wash bottles. The large end of the tube is loosely stoppered by inserting an alundum crucible of the proper size. The wash bottles are connected by means of rubber tubing. A rubber stopper on the end of a bent glass tube connects the small end of the combustion tube with the first wash bottle. The last wash bottle is attached to a

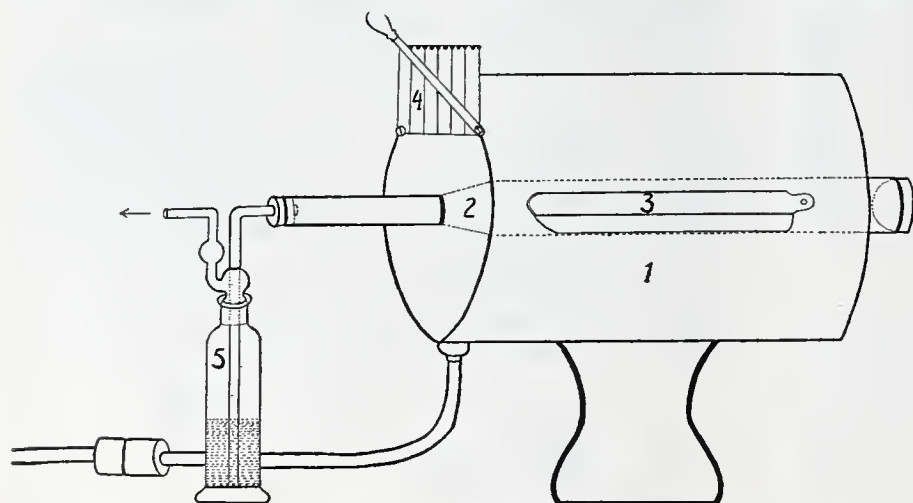


FIGURE 1. FURNACE READY FOR USE

TABLE I. RESULTS OF DETERMINATION OF IODINE IN SOILS BY THREE METHODS

LABORATORY SOIL No.	ANDREW'S METHOD	VON FELLENBERG'S METHOD	COMBUSTION METHOD	LABORATORY SOIL No.	ANDREW'S METHOD	VON FELLENBERG'S METHOD	COMBUSTION METHOD
	P. p. b.	P. p. b.	P. p. b.		P. p. b.	P. p. b.	P. p. b.
98103—Mercer Co., Ky.	3060	4020	3730	98288—Mercer Co., Ky.	4500	4530	5600
	3800	4050	3800		4500	5600	5455
	4000	4150			4760	5660	5295
		4115				5750	
	Av. 3620	4083	3765		Av. 4587	5610	5450
98110—Mercer Co., Ky.	5000	5700	5640	98293—Mercer Co., Ky.	4560	5250	5300
	4819	5640	5800		4700	5355	5050
	4734	5580	5400		4750	5560	5400
	Av. 4851	5640	5613		Av. 4670	5388	5250
98190—Mercer Co., Ky.	3500	4200	4000	98296—Mercer Co., Ky. New Jersey	3500	3600	3480
	3500	4230	4000		7800	7000	6766
	3340	4010	4120		7000	7200	6823
	Av. 3447	4146	4040		6950	7160	7000
98282—Mercer Co., Ky.	3840	5500	5600	South Carolina	Av. 7250	7120	6863
	3630	6100	5400		2515	3200	3120
	3200	6000	5400		3000		
	Av. 3556	5866	5466		Av. 2757	3200	3120
98284—Mercer Co., Ky.	3390	3500	3320	Canada	2000	2240	2700
	3590	3545	2950		2100	2300	2790
	4760				2136	2700	2895
	Av. 3913	3522	3135			2800	
98285—Mercer Co., Ky.	7100	8000	8000	J. Stoll's farm, Fayette County, Ky.	Av. 2079	2510	2795
	7300	8100	8150		0000	0000	Blank
	7300	8120			0000	Trace	200
	7320				0000	0000	110
	Av. 7255	8073	8075		Av.		103
98286—Mercer Co., Ky.	5600	8350	8500	T. B. Beard, Farm No. 3, Breck- enridge Co., Ky.	..	2610	2400
	5750	8050	8000				
	5950	8550		Hardinsburg, No. 1, Breckenridge Co., Ky.	4100	5060	4820
	6240	8560			4310	4958	4900
	6450				4015	5190	4700
	6360				Av. 4141	5069	4806
	Av. 6058	8377	8250				

suction pump which draws air through the apparatus during the combustion.

A rheostat controls the rate of heating the furnace. About 2 hours are required to bring the furnace to the maximum temperature of 1100° C., and the sample is heated for about 2 hours after the furnace reaches the maximum temperature. The current is then disconnected and the furnace allowed to cool. The solution in the wash bottles is rinsed into a porcelain dish and evaporated to dryness. The residue is dissolved in a few cubic centimeters of hot water and filtered into a small porcelain dish, evaporated to dryness again, and ignited gently to destroy the small amount of organic matter usually present. When cool, the residue is dissolved in a few drops of hot water, filtered into a separatory funnel, and pure 95 per cent ethyl alcohol is added until a layer stands on top of the aqueous solution. After being shaken vigorously for about 2 minutes, the two layers of solution are allowed to separate, the aqueous layer is run into an empty separatory funnel, and the extraction repeated twice. The residue from evaporating the alcoholic solution to dryness is dissolved in a few drops of water and transferred to a small separatory funnel, a few drops of sulfurous acid are added, and the funnel is stoppered and shaken. Then 1 cc. of carbon disulfide and approximately 1 cc. each of 1 to 1 sulfuric acid and 10 per cent sodium nitrite solution are added, and the funnel is shaken vigorously for about 2 minutes. If the carbon disulfide is colored pink it is allowed to stand awhile, after which a portion is compared in a microcolorimeter with an iodine standard treated in the same way. The iodine content is calculated to parts per billion, or milligrams per kilogram.

To ascertain the accuracy of the combustion method in comparison with the methods of Andrew (1) and von Fellenberg (2), a considerable number of duplicate determinations were made on several different soils by each of these methods. The results are contained in Table I.

The Andrew method consists in heating gently in a nickel dish 1 gram of soil to which 1 cc. of a saturated solution of potassium carbonate has been added, until all of the water is expelled and the organic matter contained in the soil has

been destroyed. After cooling, the residue is digested in hot water, the solution is boiled and filtered, and the insoluble residue washed twice. The filtrate is evaporated to dryness and ignited gently, and the residue is cooled and extracted with 90 per cent alcohol. The alcoholic extract is evaporated to dryness, the residue taken up in a few drops of water, transferred to a separatory funnel, iodine is liberated in the usual way and absorbed in chloroform, and the color compared with an iodine standard treated in a like manner.

The von Fellenberg method consists in adding 6 grams of potassium hydroxide and a little water to 2 grams of finely pulverized soil in an iron crucible and heating cautiously until the water has been expelled and the silicates are completely decomposed by fusion. The fused mass is slaked with enough water to form a sludge of the alkaline silicates. A small quantity of a saturated solution of sulfurous acid is added and the silicate sludge made acid by the addition of hydrochloric acid to decompose the alkaline silicates. The silicate sludge is then made distinctly alkaline by the addition of a saturated solution of potassium carbonate. The alkaline mass of silicates is evaporated¹ to a pasty consistency and the iodide removed by repeated extractions with alcohol. The alcoholic extract is evaporated to dryness and iodine determined in the residue either colorimetrically or by titration with a standard solution of thiosulfate.

DISCUSSION OF RESULTS

The results for the iodine content of several different samples of soils by three different methods show that the von Fellenberg method gave slightly higher figures in most instances

¹ At this point the authors have found it advantageous to modify the von Fellenberg method as follows: After making the sludge alkaline by the addition of a saturated solution of potassium carbonate, the mass of silicate is transferred onto a folded filter and thoroughly washed with hot water. The filtrate is evaporated to the point where soluble salts begin to crystallize out. The solution is then transferred and rinsed into a separatory funnel. Pure 95 per cent ethyl alcohol is added, the mixture vigorously shaken, the aqueous solution separated, and the extraction repeated twice. The alcoholic extract is evaporated to dryness and the iodine determined in the residue.

than the combustion method, but the differences are not material. Only three of the fifteen samples gave a higher result by the Andrew method than by the combustion method, and in only two of the samples slightly higher figures were obtained by the Andrew method than by the method of von Fellenberg.

From the procedure described in the Andrew method, we would not expect total iodine to be obtained because all of the silicates would not be decomposed by the low heat applied in the fusion procedure. Andrew states that in no case was he able to recover more than 60 to 70 per cent of the total iodine present, and attributes this to losses from overheating. It is possible, however, that the low results obtained by the Andrew method are due in part, at least, to incomplete decomposition of the soil silicates. Andrew further states that as a result of his experimental work it was concluded that there are no practical means of improving the extraction of iodine, but that, if the amount of iodine obtained is increased by one-half, this quantity is a true indication of the iodine content of the soil. From the results which have been obtained by the three methods the authors do not concur in this opinion. It is true that serious losses may occur from overheating and possibly other unrecognized causes as well in both the Andrew and von Fellenberg methods, but the authors are of the opinion that as much as 95 per cent recovery of the total iodine content of soils is possible by either the von Fellenberg or the combustion method.

The principal advantage of the combustion method is that the tedious manipulations of extracting a small quantity of iodine from a relatively large mass of silicate material is obviated. It requires about 2 hours to make a combustion after the furnace has attained the maximum temperature. By having several combustion boats, it is possible to run samples continuously by removing the ignited sample and inserting a fresh portion without allowing the furnace to cool. In this way it is possible to make three combustions per day with a single-tube furnace. Since electric furnaces carrying as many as four tubes are on the market, it is possible to increase the number of determinations per day accordingly.

To ascertain if iodine was retained by the soil after ignition in the electric furnace, 5-gram portions were finely ground and fused in an iron crucible with potassium hydroxide according to the method of von Fellenberg (2), but no iodine was found. These tests convinced the authors that iodine can be completely volatilized at 1100° C. from residual soils such as occur in Kentucky.

To ascertain if the iodine volatilized was uncombined, a solution of water-soluble starch was placed in the gas wash bottles and a distillation made in the usual way. The starch solution was not colored blue. However, the sensitivity of this test is probably less than the small quantity of iodine which can be determined colorimetrically by the carbon disulfide method.

After several trials the authors have discarded the titrimetric method of determining small quantities of iodine and concur in the statement made by Andrew—namely, "One is adding very many times the quantity of the substance for which one is looking and there is always a risk of decomposition of the KI and the liberation of an excess of iodine." For these reasons results have been obtained by absorbing the iodine in carbon disulfide, centrifuging any occasional turbid solution until clear, and making the comparisons with a freshly prepared iodine standard in a microcolorimeter. With these precautions and by a considerable number of duplications, these determinations represent at least 95 per cent recovery of the total iodine present.

The amount of current used in making a determination was about 6 kw-hr. This makes the cost for current in this laboratory about 20 cents a determination.

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RECEIVED April 15, 1931. Presented before the Division of Agricultural and Food Chemistry at the 80th Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931. Published by permission of the Director, Kentucky Agricultural Experiment Station.

Effect of Temperature on Sulfuric Acid Method for Lignin

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IN A preceding paper (1) it was pointed out that the sulfuric acid method for the determination of lignin gave values considerably higher for the cornstalk than did the Willstätter method. A similar discrepancy for flax and hemp has been reported by Schwalbe and Becker (3). As analytical data for the cornstalk accumulated over a three-year period, it was observed that the lignin values obtained in the summer were consistently higher than the values obtained in the winter. Since this variation was observed in the results of independent workers in spite of every effort at uniformity in the method, it was concluded to be caused by the seasonal variation in temperature.

Direct experiment not only proved that the values obtained for lignin by the 72 per cent sulfuric acid method depend upon the temperature at which the analysis is made, but also revealed the fact that the difficulty of filtration frequently encountered in this analysis is also due to the higher temperatures.

ANALYTICAL PROCEDURE

The lignocellulose materials were prepared for these analyses by grinding in a Wiley mill fitted with a 60-mesh screen. After the grinding, the wood samples were dried in a vacuum oven at 60° C. and then extracted with alcohol-benzene mixture to remove the resins and waxes. The alcohol-benzene extraction was omitted in the case of the cornstalk materials and pulps, since these materials contain very little extractable matter.

Two-gram samples were taken for analysis. The determination was carried out as reported by Schorger (2), except that instead of standing at room temperatures the samples were placed in compartments at controlled temperatures. The sulfuric acid was 72.6 per cent by analysis. The samples were weighed out and placed in 150-cc. beakers within a desiccator placed in the compartment at the desired temperature. When the samples and the acid had come to the proper temperature, 30 cc. of the acid were slowly poured

into the beakers containing the samples and the contents stirred until uniform. The samples were then left, with occasional stirring, at the constant temperature for 18 hours.

At the expiration of 18 hours, the samples were removed from the constant-temperature apparatus, made up to 1200 cc. with water, and gently boiled for 2 hours. After the flocculent precipitate had settled, the material was filtered through a prepared Gooch crucible, washed with hot water until free of sulfates, dried at 105° C., cooled, and weighed. The carbonaceous matter was burned in a muffle furnace, and the crucibles cooled and weighed again. The loss in weight was taken as lignin.

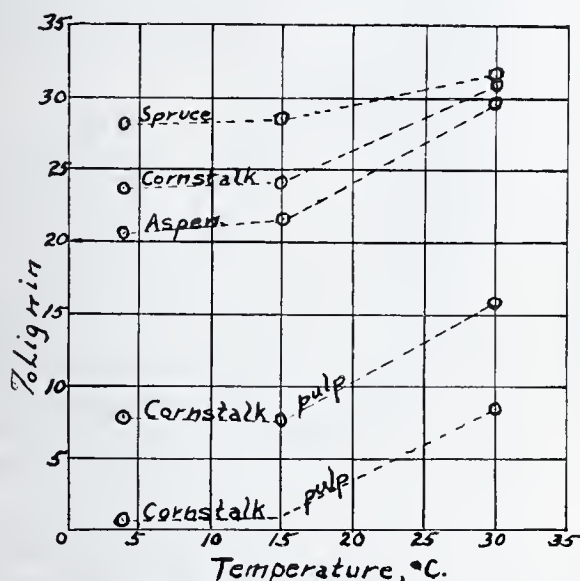


FIGURE 1. EFFECT OF TEMPERATURE ON PER CENT OF LIGNIN AS DETERMINED BY SULFURIC ACID METHOD

The lignin in several lignocelluloses was determined by this procedure at temperatures of 30°, 15° C., and at an "ice box temperature" which was practically constant at 4° C. The lignin values were also obtained by the Willstätter hydrochloric acid method in order to have values representative of different methods of lignin determination. The results are reported in Table I and shown graphically in Figure 1. All results are reported on the dry basis.

TABLE I. COMPARISON OF LIGNIN VALUES OBTAINED BY 72 PER CENT SULFURIC ACID METHOD AT VARIOUS TEMPERATURES AND BY WILLSTÄTTER HCl METHOD

MATERIAL	MOISTURE	72% SULFURIC ACID METHOD At 30° C. At 15° C. At 4° C.	WILLSTÄTTER HCl METHOD
Spruce wood	2.5	31.40 28.35 28.05	27.70
Aspen wood	5.2	29.55 21.50 20.45	20.00
Total cornstalk	7.9	30.80 24.00 23.70	22.80
Cornstalk pulp; NaOH process		15.70 7.60 7.70	7.50
Cornstalk pulp; NaOH process		8.30 0.60	
Cornstalk, outer, shell	7.6	33.50 ^a 25.20	25.40
Cornstalk, vascular bundles	8.0	35.20 ^a 22.50	22.00
Cornstalk pith	8.3	32.00 ^a 16.50	15.90
Cornstalk pith mechanically separated	8.4	28.01 ^a 19.72	19.50

^a Made at room temperatures during summer months before significance of temperature was noted. Although no record of laboratory temperature is available, it may be stated as between 30° and 37° C.

DISCUSSION OF RESULTS

The data in Table I indicate that the temperature has a very great effect upon the values obtained for lignin in lignocelluloses when determined by the 72 per cent sulfuric acid method. In the case of cornstalks, the variation is from 23.7 per cent at 4° C. to 30.8 per cent at 30° C. The variation in the case of the spruce wood is not so great, but with aspen there is a variation from 20.45 to 29.55 per cent. This would indicate that in the use of the 72 per cent sulfuric acid method for the determination of lignin, the tempera-

ture for the hydrolysis of the carbohydrate material should be kept at least below 15° and preferably at about 4° C., or the temperature obtainable in an ordinary ice box.

The effect of temperature upon the character of the lignin residue is indicated by the fact that at 4° and 15° C. a residue is obtained which is comparatively easy to filter and is of a light brown color. The residue obtained at 30° C. is black in color and of such fine semi-colloidal nature that filtration is very difficult.

A possible explanation for the increase in lignin value with increase in temperature is the increased carbonization of the hydrolyzed carbohydrates at the higher temperatures. If this were the case, the variation in lignin values of those materials low in lignin should be more pronounced than the variation in those lignocelluloses high in lignin, as there would be a larger percentage of carbohydrate material hydrolyzed in comparison to the amount of lignin present. An examination of the data shows this to be the case. With the cornstalk pulp containing very little lignin, the increase is some 1280 per cent, whereas with a cornstalk pulp of high lignin value, the increase is 100 per cent, and with the original lignocelluloses the increase is from 44.5 with aspen wood to 30.0 per cent with cornstalks.

This conclusion is also supported by the data in Table II showing the increased percentage of carbon found in the lignin obtained by treating the cornstalk at 30° C. as compared to similar lignin prepared at 4° C. It should be noted that there was no appreciable difference in the percentage of sulfur in the lignin, a fact which eliminates the possibility of the difference being due to sulfonation of the lignin.

TABLE II. CARBON, HYDROGEN, AND SULFUR ANALYSIS ON LIGNIN

(Obtained from cornstalk at various temperatures by 72% sulfuric acid method)

TEMP. OF LIGNIN PREPARATION ° C.	CARBON %	HYDROGEN %	SULFUR %
30	62.2	4.94	0.31
30	62.1	5.33	0.78
4	61.4	5.82	0.04
4	61.3	5.77	Trace

Laboratory temperatures will vary from 18° to 40° C. in this vicinity according to season. The data presented clearly show that the 72 per cent sulfuric acid method for lignin would have little significance if carried out at such varied "room temperatures." In standardizing a temperature for the determination, one conveniently attained in any laboratory should be selected, although the data indicate little change in results between 4° and 15° C. The temperature of the ice box suggests itself as the most convenient practical solution of the problem. The procedures as described in the literature (2) would need no change, except that the sample and reagent should be cooled to these temperatures before mixing and then kept at this temperature in a closed container for the prescribed 18 hours for hydrolysis of the carbohydrates.

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RECEIVED November 9, 1931.

TO INCREASE ALCOHOL CONSUMPTION, the Italian Government has decreed that importers of gasoline secure locally 428 liters of water-free spirits for each hundred quintals (3170 gallons), and mix these so that a certain portion of the finished product will comprise 20 per cent alcohol and 80 per cent benzene.

High-Precision Constant-Temperature Bath

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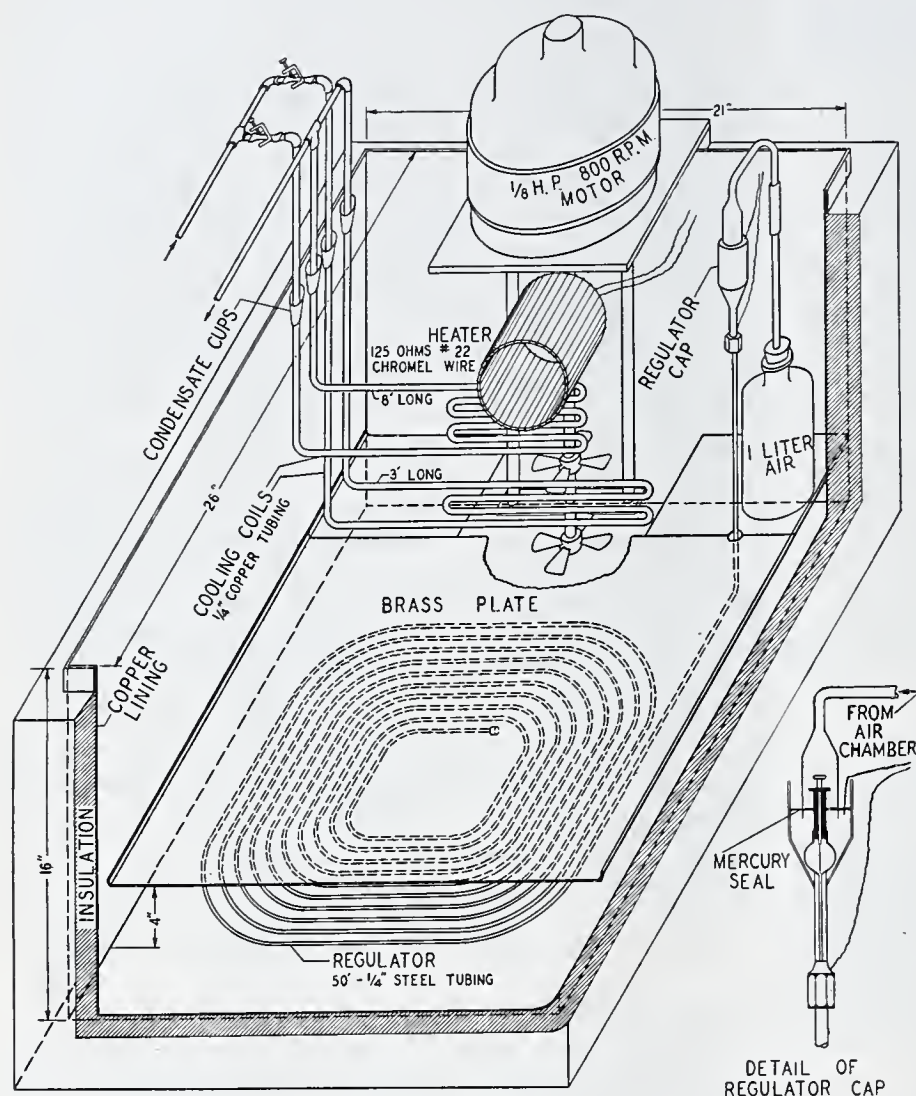


FIGURE 1. DIAGRAM OF APPARATUS

THE temperature-control system herein described is the culmination of developments in this laboratory which have extended over the last 20 years. The objective has been to construct a system such that every part would function continuously without attention over a period of many months and maintain a temperature constant throughout the whole period to less than 0.01°C . maximum variation, and which would operate over shorter periods to within 0.001°C . Those who have had occasion to maintain accurate temperature control over long periods of time are familiar with various exasperating factors, such as breaking of belts, fluctuation of temperature of room or of the cooling water, sticking of relay contacts, fouling of regulator contacts, failure of dry cells or storage batteries, burning out of heating elements, electrical leaks, lags in the controlling system, gradual creeping of temperature, etc. The system described has been in use now for about 2 years, and during that period has remained free from these disturbing factors.

A satisfactory thermostat must consist of a suitable container, well insulated thermally. The bath liquid should be transparent, nonvolatile, of low viscosity and electrical conductivity, but of high specific heat. The stirring apparatus must keep all parts of the bath at the same temperature.

The cooling and heating systems must take care of all fluctuations in room temperature with no time lag. The thermoregulator and control system must respond instantly to minute temperature changes, must not be affected by outside factors, must be automatic, and must not require readjustment.

The essential parts of the apparatus are represented in Figure 1. The bath liquid is petrolatum, an odorless, transparent mineral oil of fairly low viscosity and low electrical conductivity. A variable external resistance allows adjustment of the heating current.

The efficiency of stirring is appreciably increased by a metal plate mounted as indicated. The oil makes a complete circuit in from 10 to 15 seconds. This system keeps the temperature of all parts of the bath the same within the limits of reading a Bechmann thermometer.

Although the relative coefficient of expansion of mercury in steel is much smaller than that of toluene in glass, which is another widely used type of regulator, yet the much higher heat conductivity and lower specific heat of mercury and of steel, and the thin wall of the steel tubing make the mercury regulator the more desirable. The large surface of thin-walled metal tubing reduces time lag to a negligible quantity.

The regulator was filled slowly under a high vacuum. The upper end was fastened to a vacuum oil pump, and the lower end, fitted with a metal cap through which an extremely small hole had been drilled, was placed under mercury. It was insulated from the bottom of the bath by glass cups. The top of the regulator

terminates in a glass capillary tube cemented to the steel tube and fitted with a metal cap through which passes a thin steel machine screw of extremely fine thread. This steel pin makes

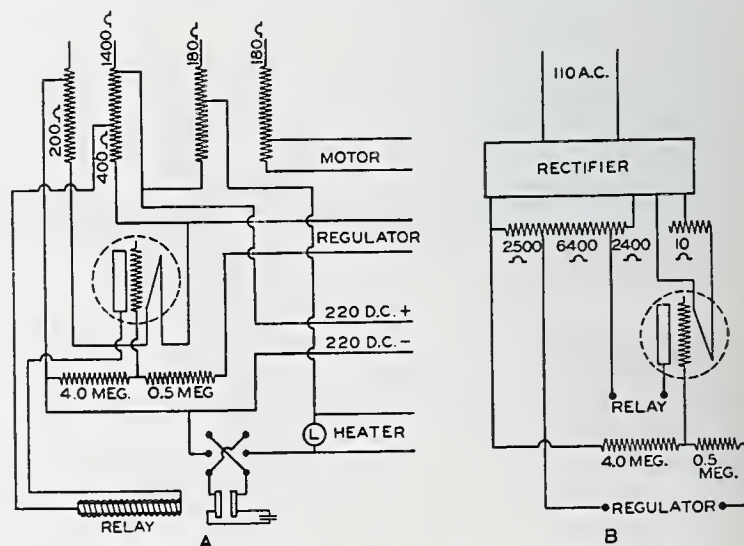


FIGURE 2. WIRING DIAGRAMS EMPLOYING 220 VOLTS D.C. AND 110 VOLTS A.C., RESPECTIVELY

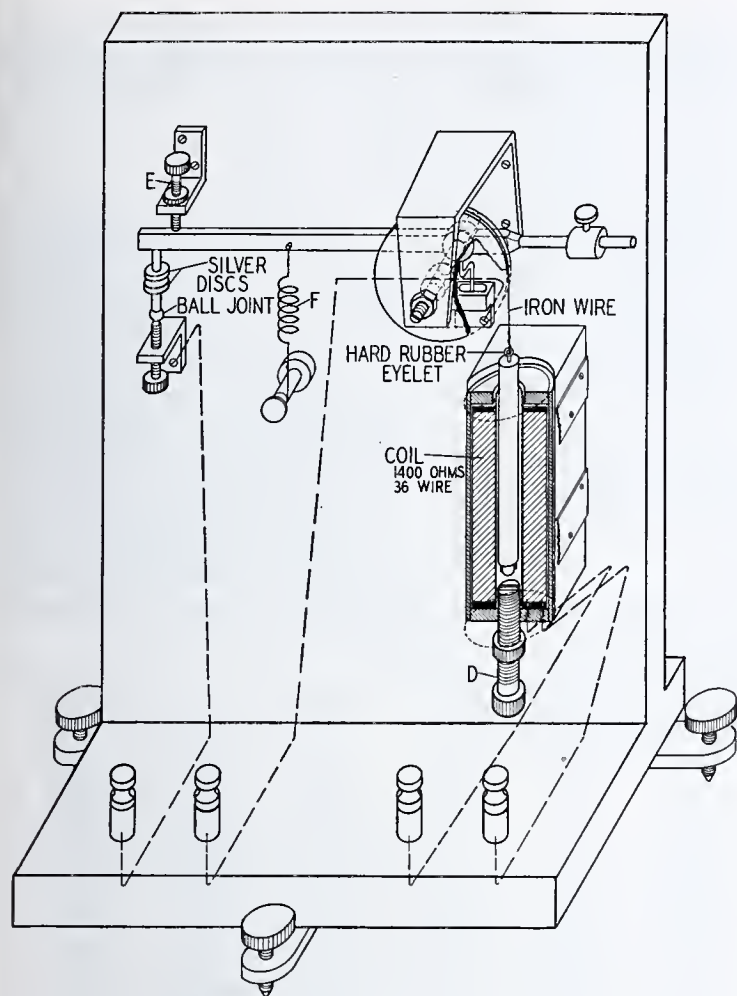


FIGURE 3. DIAGRAM OF RELAY

contact with the mercury just at the point where the glass capillary opens into a small bulb.

It appears to be impossible to remove the last traces of air from the regulator. When the thermostat was first operated, a correlation was observed between barometric pressure and temperature of the bath. To eliminate this disturbing factor an arrangement was constructed to keep the mercury surface in the regulator under nearly constant pressure. A 1-liter bottle filled with air was placed in the constant-temperature bath. This was connected through a capillary tube to a wider tube which fitted over the regulator top and into a mercury seal, as shown in the detail drawing. Changes in barometric pressure produce practically no change in pressure within the bottle and thus upon the mercury in the regulator. This device eliminates entirely the influence of changes in barometric pressure.

Automatic control is accomplished by the use of the vacuum tube set-up of Beaver (1) adapted to the X '71A tube. Since in this system only 10 microamperes flow through the regulator, there is no sparking and thus no oxidation of the mercury surface.

The X '71A tube is well adapted for this purpose since, with a filament current of only 0.20 ampere, zero grid potential, and 75 volts plate potential, a plate current of 12 milliamperes, which is much more than is required to operate the relay, is produced. A negative grid potential of 25 volts reduces the plate current to zero, an absolutely essential feature. Two X '71A tubes on separate thermostats have been in constant use for 18 months with little sign of deterioration.

Two wiring diagrams are shown in Figure 2. System A employs 220 volts d. c. and is a modified form of the one described by Beaver. It will be seen that 110 volts d. c. could be used equally well. System B uses 110 volts a. c. in conjunction with a radio A. B. C. power pack which contains

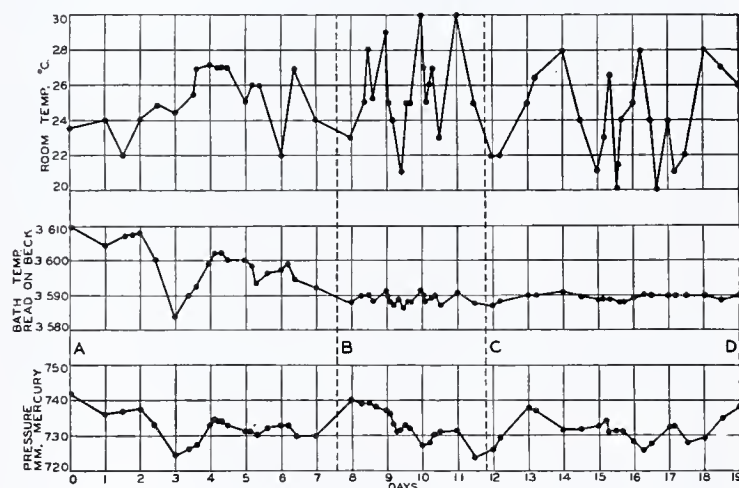
an X '80 full wave-rectifier tube. Both systems have been in use interchangeably with equal satisfaction.

The essential features of the relay used are represented in Figure 3. The soft-iron core of the electromagnet is covered with thin paper to prevent sticking to the thin brass tube upon which the wire is wound. The bottom of the plunger is cut away as shown, and the depression filled with several layers of paper to prevent sticking at the lower edge. Adjustment is made by means of the soft-iron set screw *D* in the bottom of the electromagnet, the stop *E*, the adjustable spring *F*, and the counterbalance weight.

The relay is extremely sensitive. With a coarse adjustment it operates over a range of from 7 to 25 milliamperes, but can readily be made to operate over a range of from 2 to 12 milliamperes.

The system is so sensitive that the relay operates with a continuous chatter. This can be prevented by means of a small condenser across the 4-megohm resistance in Figure 2. A 0.02-mf. condenser causes the relay to operate about once a second. The reliability of the instrument is demonstrated by the fact that one has been used continuously for more than a year without a single adjustment.

When the thermostat was first operated, a record was made of room temperature, barometric pressure, and thermostat temperature. The results are represented graphically in Figure 4. The lower curve shows the fluctuations in pressure,

FIGURE 4. BATH TEMPERATURE *vs.* BAROMETRIC PRESSURE BEFORE AND AFTER APPLICATION OF CONSTANT-PRESSURE DEVICE, AND BATH TEMPERATURE *vs.* ROOM TEMPERATURE

the center one fluctuations in thermostat temperature, and the upper one the changes in room temperature. The correlation between thermostat temperature and barometric pressure is evident over the portion of the curve from *A* to *B*. At the point *B* the constant-pressure device was attached. It will be observed that this eliminated the influence of pressure. From *B* to *C*, however, there is a slight change in thermostat temperature with room temperature. At the point *C* the rate of heating and cooling was increased. This eliminated the influence of changes in room temperature. Under these conditions the temperature of the bath can be held constant for days within the limits of error of reading a Bechmann thermometer. Since, however, such accurate temperature control is usually not necessary, the customary operating conditions are best represented by the center section of the curves.

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RECEIVED July 28, 1931.

Detection of Sulfite Waste Liquor in Sea Water

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CONSIDERABLE work has been done on the effect of sulfite pulp mill effluent on fresh water streams. Investigations in Wisconsin (12) describe various technical methods which have been developed to measure the efficiency of ponding of sulfite wastes. In a recent sanitary survey of the Willamette Valley in Oregon the measurement of sulfite pollution is also undertaken (7). Quite generally the greatest reliance has been placed upon the biochemical oxygen demand and the oxygen consumed values as indicators of the presence of unstable organic matter, any appreciable increase in the vicinity of pulp mills being attributed to their effluent. In some cases use has been made of plants and animals as indicators (10) of the nature of polluting matter.

The detection of sulfite waste liquor in sea water is complicated by several factors. The presence of tidal currents and eddies and the higher density of sea water in relation to fresh water are liable to make sampling highly erratic unless taken over a long period of time. The organic content of sea water is also extremely variable, depending upon its relation to the larger ocean waters as well as to the land drainage. It contains both calcium and sulfate ions. The presence of sulfite waste liquor in sea water, unless in great quantity, cannot be detected, therefore, by simple chemical analysis. In the absence of a specific test, it is evident that its presence or absence in sea water must be established by a number of corroborative tests rather than by the simpler determinations used in studies of fresh-water pollution. Therefore, it is of interest to consider the use of various methods which may be applied to the quantitative estimation of sulfite waste liquor in sea water.

OXYGEN BALANCE

In a previous paper (1) the usual biochemical oxygen demand of sea-water samples suspected of containing sulfite waste was subtracted from the dissolved oxygen contained in a sample taken simultaneously. The result obtained was known as the oxygen balance. In samples of unpolluted sea water the oxygen balance approaches the dissolved oxygen in value, whereas in polluted water its value is negative—i. e., the oxygen required to oxidize the polluting matter is greater than that contained in the sample as dissolved oxygen. By calibrating this measure with representative samples of sulfite waste taken from the digester just prior to the blowing of the digester, it was found that a concentration of one part of sulfite liquor in 7500 parts of sea water (133 parts per million) will yield negative values. It is still sensitive at dilutions of one in 30,000 (33 $\frac{1}{3}$ parts per million). By comparing the oxygen balance of an unpolluted sea water in the same locality with that of the sample, it is evident that the difference must be due to the extraneous or polluting matter.

In dilute concentrations of sulfite waste liquor in sea water, the oxygen consumed and the biochemical oxygen demand values, when compared with similar values for an unpolluted sea water in the same locality, are useful indicators of its presence.

With the aid of an accurate colorimeter, pH values vary in the same manner as the equivalent acid required to give a constant pH beyond the buffering range of sea water.

For high concentrations, the ordinary analytical determinations, such as dissolved oxygen, sulfates, and, to some extent, color, may be used to give approximate indications of amounts of sulfite waste liquor present, if compared with a suitable reference sample.

Objection to this method lies in the variation of naturally occurring oxidizable organic matter in unpolluted sea water due to the change of tide or to land drainage. Another objection consists in the decrease of dissolved oxygen due to the polluting matter. Nevertheless, the oxygen balance furnishes a graphic representation of the spread of pollution over a given area when sufficient samples are taken.

BIOCHEMICAL OXYGEN DEMAND AND OXYGEN CONSUMED VALUES

The same result may of course be obtained by using the oxygen demand itself. When the 5-day demand at 25° C. is divided by the sewage factor 0.68, a set of values is obtained which, when plotted against various concentrations of digester liquor in sea water, rather closely parallels that obtained by the proposed modification (2) of the permanganate method for oxygen consumed. A study of Figure 2 together with the close agreement on samples of sea water indicates that both methods are sensitive within the range of one part of digester liquor in 5000 to 20,000 parts of sea water.

HYDROGEN-ION CONCENTRATION

Sulfite waste liquor varies considerably with the methods used for pulp digestion. The method of sampling also has a marked effect on the analytical constants. If it is taken from the blow pit it has been diluted by the cooling showers generally employed, and if it is blown hot from the digester it suffers loss of SO₂. To eliminate these variables and to obtain maximum pollutorial effects, cold-drawn samples from digesters were used. Even so, the liquor from two different mills shows variations in composition as given in Table I.

TABLE I. COMPOSITION OF SULFITE WASTE LIQUOR

	SAMPLE A	SAMPLE B
	%	%
Total SO ₂	1.11	0.47
Total solids	10.59	11.11
Volatile solids	9.44	10.17
Ash	0.94	1.15

The acidic nature of digester liquor, due to its slight content of free SO₂, will of course reduce the alkalinity of sea water. Its pH value should therefore be a measure of its presence, and in fresh water such values are commonly accepted for its determination. In sea water, however, the accuracy of pH values has been questioned. It has been shown by Irvine (5) that bicarbonate ions, as well as minute traces of phosphates, borates, silicates, and organic matter, exert a buffering effect and that a relatively large addition of acid is necessary to alter materially the pH of such a buffered solution, especially between pH 5.5 and 8. Therefore, various investigators (3, 6) have proposed to set free the CO₂ by adding acid to increase the hydrogen-ion concentration to 10⁻⁴ grams per liter and thus get beyond the range of the buffering effect. By titrat-

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ing 100 cc. of sea water with 0.01 *N* hydrochloric acid, using a convenient indicator until the color changes, and expelling the carbon dioxide, it has been found that ocean water requires from 23 to 26 cc. of 0.01 *N* acid to bring it to a hydrogen-ion concentration of 10^{-4} grams per liter. As an alternative (8) the sea water may be titrated until the color of the indicator is the same as at the same concentration in distilled water saturated with carbon dioxide. The amount of acid necessary to yield a constant pH of approximately 4.0 should therefore be a measure of other acidic constituents not normally present in ocean water.

In Table II are given values obtained by various dilutions of digester liquor in sea water, in distilled water, in distilled water saturated with carbon dioxide, and the amount of acid required to bring the sea water dilutions to a constant pH of 3.7. All determinations were made by means of a Bausch and Lomb hydrogen-ion colorimeter, the dilutions being made by means of a microburet and kept in Pyrex bottles.

TABLE II. pH OF DIGESTER LIQUOR DILUTIONS IN STABILIZED SEA WATER

DIGESTER LIQUOR P. p. m.	SAMPLE A pH	SAMPLE B pH	0.01 N ACID FOR pH 3.7 Cc.	DISTILLED WATER pH	DISTILLED H ₂ O AND CO ₂ pH
10,000	3.34	4.97	5.9	2.85 ^a	2.85 ^a
8,000	3.50	5.69	10.3	2.96	2.92
6,000	3.86	6.17	15.0	3.14	3.12
4,000	5.66	6.34	16.0	3.65	3.24
2,000	6.64	6.72	20.9	3.68	3.56
1,000	6.95	6.99	21.5	4.00	3.89
800	7.05	7.06	25.0	4.17	3.99
600	7.21	7.07	25.0	4.46	4.11
400	7.06	7.15	25.0	4.85	4.20
200	7.37	7.34	25.0	5.43	4.30
100	7.60	7.60	25.1	6.23	4.36
80	7.59	7.61	25.1	6.68	4.43
40	7.85	7.68	25.3	6.68	4.36
25	7.70	7.79	25.3	6.68	4.43
Blank	7.79	7.82	25.3	6.68	4.40

^a Matched in colorimeter and estimated.

These values are plotted in Figure 1 on semi-logarithmic paper. It is noted that in both sea water and distilled water the pH and acid equivalent values are noticeably affected in the dilution of 200 parts per million (one part in 5000 parts) and that the general shape of these curves is the same. Below 100 parts per million changes in pH are apparently within the range of experimental error. In the higher concentrations, the respective values for pH and equivalent acid show a marked proportionality to the dilution values in sea water. From the similarity of the graphs, there seems to be no necessity for correction of the buffering action of sea water, since the changes in pH are of the same order regardless of its range or the presence or absence of buffering agents. In sulfite liquor-disposal systems, direct readings of pH should therefore continue to be a very simple and accurate means for the detection of sulfite liquor where it is known to be the polluting agent and where reference values for the unpolluted water of a given locality have been determined simultaneously.

TABLE III. BUFFERING ACTION OF ORGANIC MATTER IN SEA WATER

ORGANIC MATTER	pH	0.1 N HCl ADDED Cc.	RESULTANT pH
Blank sea water	7.95	25.0	3.69
Coffee	7.55	25.0	3.98
Compost	7.81	25.0	3.83
Cider	6.98	25.0	3.74
Milk	6.06	20.0	4.45

It is of interest to note the effect of organic matter in general upon the buffering action of sea water. For this purpose various organic substances ordinarily associated with the use of land draining toward the sea, such as orchard and dairy products, vegetable extract, and decaying matter, were added to stabilized sea water and allowed to undergo fermentation.

In Table III are given the values obtained on adding one cup of breakfast coffee, sweet cider, fresh milk, and garden compost (leaves, humus), respectively, to a quart of stabilized sea water. The mixture was kept in an open Mason jar at a temperature of 70° F. for 2 weeks. After filtration, dilutions of 10,000 parts per million of stabilized sea water were made of the respective solutions.

It is apparent that old organic matter in sea water such as results from animal and vegetable matter lowers the pH and affects the buffering of sea water to an appreciable degree.

SULFATE-CHLORIDE RATIO

The ratio of the sulfate and chloride content of the waters of North Puget Sound has been investigated by Thompson (11) and found to have a constant value of 0.1396. In the larger bodies of water this value is independent of temperature and dilution variations. Further inland the value is subject to slight changes. If a polluting substance containing sulfur is added to sea water this ratio will be higher, or, if reducing substances are present as in brackish lagoons or over mud flats where anaerobic conditions prevail, its value will be diminished.

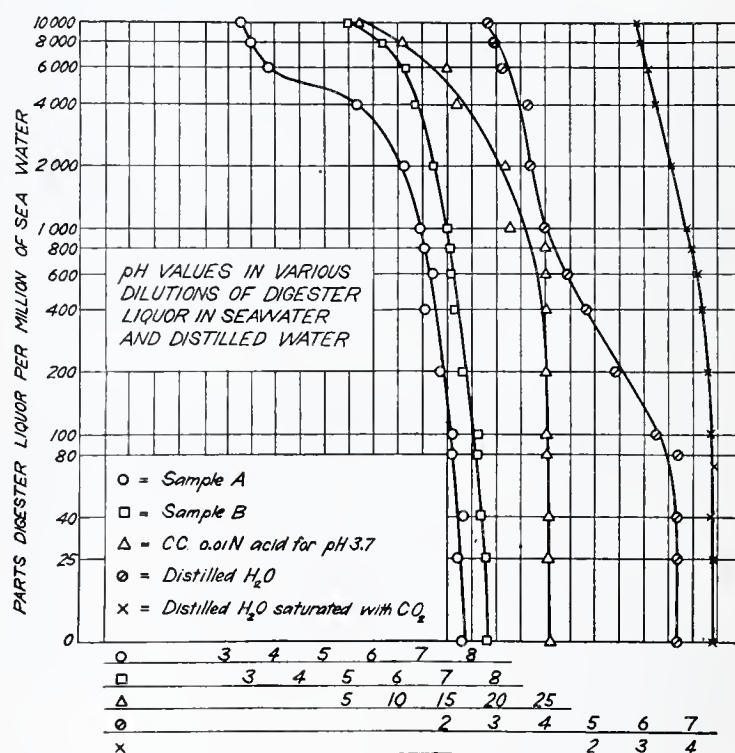


FIGURE 1

The effect of sulfite waste liquor on this ratio may be noted in the dilution studies given in Table IV, in which bromine is used as the oxidizing agent in preparing the samples for precipitation of barium sulfate.

TABLE IV. TOTAL SULFUR IN MIXTURE OF SULFITE LIQUOR AND SEA WATER

COMPOSITION OF SAMPLE	CHLORIDE Mg./liter	SO ₄ Mg./liter	RATIO SO ₄ :Cl
100 cc. blank	15,873	0.2237	0.1409
100 cc. + 0.2 cc. liquor	15,873	0.2259	0.1423
100 cc. + 0.4 cc. liquor	15,873	0.2772	0.1431
100 cc. + 0.8 cc. liquor	15,873	0.2324	0.1464
100 cc. + 1.0 cc. liquor	15,873	0.2380	0.1499
100 cc. + 2.0 cc. liquor	15,873	0.2441	0.1537
100 cc. + 4.0 cc. liquor	15,873	0.2586	0.1630

In order to check back in these analyses it is necessary to know the sulfur content of the sulfite liquor itself. Unfortunately this varies with each charge in commercial operation, depending upon the manner of blowing and cooling the

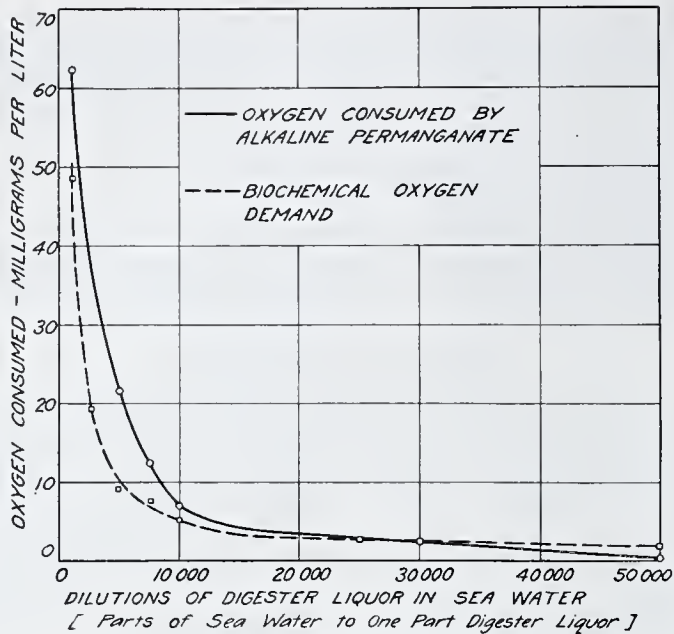


FIGURE 2. EFFECT OF SULFITE WASTE LIQUOR ON OXYGEN CONSUMED AND B. O. D. OF STABILIZED SEA WATER

sample. Even on a given sample considerable difficulty was encountered in obtaining check results. The following methods were employed: (1) Schreiber's method (9); (2) neutralization with sodium hydroxide, oxidation with bromine, and fusing the residue; (3) the method suggested by the U. S. Forest Products Laboratory, consisting of distillation of sulfur dioxide into standard iodine and precipitation of residual soluble sulfates by barium chloride; (4) the method of A. W. Schorger, suggested in correspondence, consisting of the oxidation of the organic matter by fuming nitric acid; and (5) a method in which a 10-cc. portion of diluted digester liquor (1 to 10) is taken.

In the last method, 100 cc. of bromine water are added and, after diluting to 200 cc., are digested on a steam bath overnight. Five grams of potassium chlorate and 20 cc. of concentrated hydrochloric acid are next added and the chlorine boiled off. After diluting to 400 cc., the barium sulfate is precipitated. Upon evaporating the filtrate to dryness, fusing with sodium, dissolving in hot water, and acidifying, a good test for hydrogen sulfide was obtained in each sample, showing that despite good checks in barium sulfate precipitates the method does not determine total sulfur. The results are given in Table V.

TABLE V. SULFUR CONTENT OF SULFITE WASTE LIQUOR		
METHOD	SAMPLE	TOTAL SULFUR Mg./liter
Schreiber	1	10.5
	2	10.9
Oxidation by bromine	1	8.6
U. S. Forest Products Laboratory	1	8.2
	2	8.7
	3	8.7
Oxidation by fuming nitric acid and KClO ₃	1	8.1
	2	7.7
	3	8.1
	4	8.2
	5	8.3

CALCIUM AND MAGNESIUM VALUES

The determination of calcium and magnesium in sea water requires special precautions because of the preponderance of magnesium. The results obtained by the authors are given in Table VI.

TABLE VI. CALCIUM AND MAGNESIUM VALUES

SAMPLE	Ca	Mg	Ratio Ca:Mg
	Mg./liter	Mg./liter	
Field sample of pure sea water	366.0	1128.0	0.3244
Stabilized sea water	372.3	1134.7	0.3281
Dilution 1 to 10,000	349.5	1068.5	0.3270
Dilution 1 to 1000	374.1	1068.5	0.3270
Dilution 1 to 100	392.3	1099.2	0.3569

It appears from these determinations that no appreciable effect in ionic distribution can be detected until concentrations of 1 to 100 (10,000 parts per million) are reached.

COLOR REACTIONS

Many color reactions between wood and various chemical compounds are noted in the literature (4). Some of these are regarded as being specific for lignin and it would seem reasonable that some might also apply to the soluble lignin compounds in sulfite liquor. However, the color reactions in almost every case are due to the predominance of a color-producing aldehyde in the wood. In sulfite waste liquor, such reaction has already taken place in the digester and is indeed used as a test for the completion of the cooking process. It would seem logical to conclude, therefore, that sulfite waste liquor in sea water is itself a color indicator. Hence the

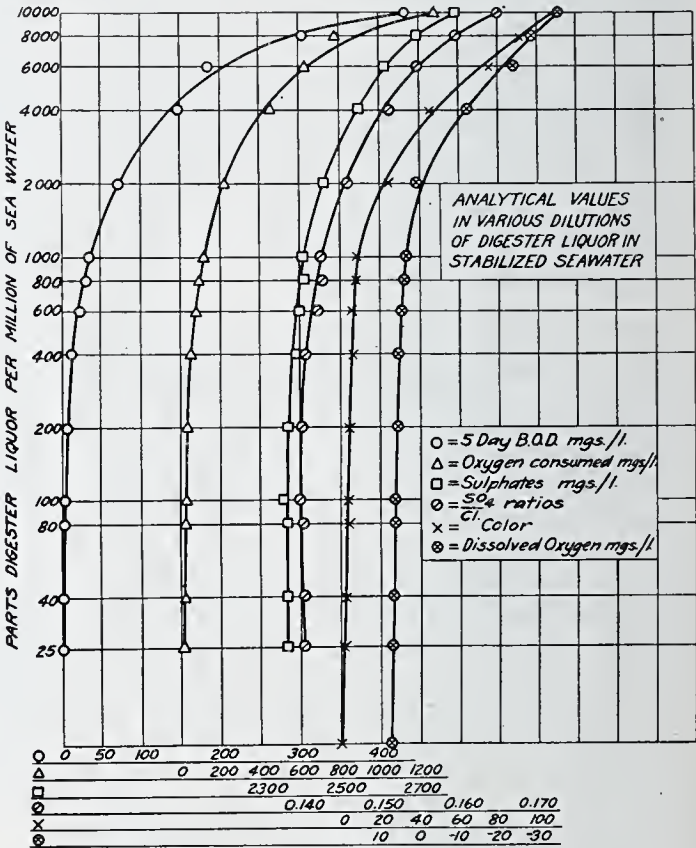


FIGURE 3

standard method for determination of color is probably as sensitive as any other reagent and is not so liable to be confused with other reactions occurring between sea water and such reagents as permanganate, chlorine, nitric acid, and ferric ferriocyanide. The color imparted to sea water by sulfite waste liquor can often be noted at the time of digester discharge for a considerable distance, and in concentrations of 1 part in a thousand (1000 parts per million) or greater it is very pronounced in laboratory samples. Caution must be exercised, however, in the interpretation of color tests in sea water. In addition to organic coloring matter brought in by stream dilution, striking color mass is often observed, and found due to phytoorganisms, as well as to organic matter from land drainage.

EFFECT OF HIGH CONCENTRATIONS

In concentrations of sulfite waste liquor exceeding 1000 parts per million, the values obtained are more marked and a wider range of determinations becomes available. In Table VII are given values determined by Standard Methods of Analysis, with the exception that oxygen consumed was made in accordance with the proposed modification. The B. O. D. was determined at 25° C. Oxidation with bromine was used for the determination of sulfates. The dilutions of the sulfite waste liquor in stabilized sea water (blank) were prepared with a micropipet. The results are the average of three dilution sets.

In Figure 3 these values are plotted on a semi-logarithmic scale and show the same general effect with increasing concentration. By comparing such values with similar values obtained from unpolluted sea water in the same locality, it is evident that a measure of the extent of pollution may be obtained.

TABLE VII. ANALYTICAL VALUES OF VARIOUS CONCENTRATIONS OF SULFITE WASTE LIQUOR IN STABILIZED SEA WATER

DIGESTER LIQUOR IN SEA WATER	DISSOLVED OXYGEN	5-DAY B. O. D.	OXYGEN CONSUMED	SULFATES	RATIO SO ₄ :Cl	COLOR PT. CO STANDARD
Parts	Mg./liter	Mg./liter	Mg./liter	Mg./liter		
10,000	-34.3	387	1295	0.2791	0.1654	112
8,000	-28.5	304	770	0.2697	0.1598	92
6,000	-24.0	169	635	0.2613	0.1549	76
4,000	-12.2	149	551	0.2551	0.1512	46
2,000	0.75	72.5	219	0.2461	0.1459	25
1,000	3.90	32.9	106	0.2400	0.1426	8
800	4.00	28.6	83.3	0.2413	0.1429	7
600	4.90	21.9	62.2	0.2398	0.1421	5
400	5.87	14.5	43.8	0.2393	0.1406	5
200	5.95	7.8	20.3	0.2362	0.1400	4
100	6.55	3.7	14.1	0.2353	0.1397	4
80	6.70	3.1	12.1	0.2367	0.1403	3
40	6.80	1.9	7.25	0.2369	0.1404	3
25	6.96	0.8	7.45	0.2372	0.1405	2
Blank	7.10	0.0	3.8	0.2381	0.1406	0

APPLICATION OF RESULTS TO FIELD MEASUREMENTS

The analytical values reported were obtained on dilutions of sulfite waste liquor in stabilized sea water. They represent

an order of magnitude rather than the correlation of sea water with sulfite waste liquor. Both of these are too variable to permit of quantitative relationships. Nevertheless, the values may be taken as approximations of sulfite waste liquor present, as is obvious from the following table:

SAMPLE	pH	COLOR	5-DAY B. O. D.	OXYGEN CONSUMED
1. Puget Sound, surface	8.1	13	1.62	2.15
2. Puget Sound, 40-ft. depth	8.1	14	0.83	2.24
3. Inland Bay, surface	8.1	12	1.35	2.38
4. Inland Bay, 16-ft. depth	8.2	13	1.14	1.94
5. Near disposal sewer of sulfite mill	7.1	90	30.15	177.6
6. 1000 parts sulfite waste per million parts of sea water (sample 3)	7.2	33	27.1	96.6

By consulting Table VII, the quantity of sulfite waste liquor in sample 5 ranges from 900 to 1500 parts per million, except that the color is much higher than the color scale of the stabilized sea water for such concentration.

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RECEIVED October 30, 1931. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

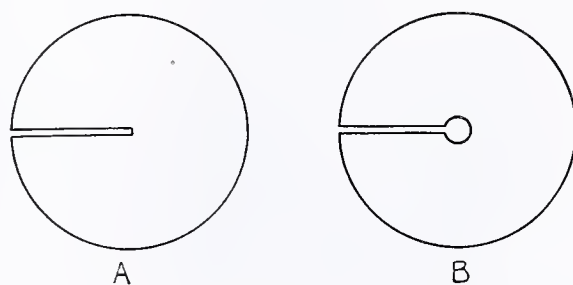
Slotted Watch Glasses for Use in Electroanalysis

EARLE R. CALEY, Frick Chemical Laboratory, Princeton University, Princeton, N. J.

FOR the prevention of loss by spraying or splashing during electrolytic determinations, the slotted watch glasses shown in the figure have been found to be a decided improvement over the perforated or split watch glasses usually employed for this purpose. Watch glasses with one or more holes drilled in them protect solutions satisfactorily during electrolysis, but the necessity of disconnecting the electrodes each time a watch glass is to be placed on or removed from a vessel renders their use inconvenient, whereas the divided type of watch glass frequently causes difficulty or loss because of its tendency to be easily jarred out of position.

The preparation of slotted watch glasses of the types shown, from plain watch glasses, presents no especial difficulty providing there is available a sufficiently thin Carborundum wheel. In making form A, which is designed for use with stationary electrodes, an ordinary watch glass is simply slotted by means of the grinding wheel. In the preparation of form B, which has been found more satisfactory for use with a rotating anode, the central hole is drilled first in the usual manner before the slotting operation is performed. In order to minimize the risk of breakage during grinding, it is necessary to select the rather thick variety of plain watch glass in preference to the thin kind.

Several practical precautions must be observed during the grinding operation in order to prepare these slotted watch glasses successfully. In the first place, the speed of the wheel should be kept low, preferably at about 400 r. p. m., and lubrication with Carborundum powder and water should be generous during the entire operation. It is quite essential to introduce the edge of the glass to the wheel slowly and to maintain a slow rate during grinding. Good technic requires



TYPES OF SLOTTED WATCH GLASSES

that the wheel be worked back and forth in the partly formed slot following each new advance so that a slight enlargement is continually produced. An average-sized watch glass should

require from 20 to 30 minutes for slotting. Finally, the glass must be held in a firm and fixed manner while grinding so that no undue strain is exerted on that portion of the slot already formed. When properly performed, the above process produces a neat clean-cut slot free from any sign of chipping.

These slotted watch glasses have been used frequently by the author and by students in this laboratory and have proved very satisfactory for covering beakers during elec-

trolytic determinations. Undoubtedly similar ones or suitable variations of them might well find application in other situations where it is desirable to provide a cover glass that may be readily removed and replaced in spite of obstructions that would otherwise interfere.

The writer wishes to acknowledge his indebtedness to E. W. Wilson, glassblower at the Frick Chemical Laboratory, for supplying the practical details of the above method.

RECEIVED November 30, 1931.

Multiple-Range Flowmeters

SAMUEL YUSTER, University of Minnesota, Minneapolis, Minn.

IN THE study of gaseous reactions by flow methods, it is often advantageous to have a multiple-range flowmeter because of the necessity of a wide range in rates of flow in the problem. In many cases the range is varied by inserting capillaries of different size by means of rubber tubing, but rubber has the disadvantage of aging and leaking, and corrosive gases attack it.

During the course of some work on halogenation, the flowmeters described in this article were designed and found to work very satisfactorily. Their ranges are changed simply by turning the stopcocks.

In Figure 1 the gas passes in at *A* and through capillary *D* or *E*, according to the range desired, and out again at *B*. By turning stopcock *C* through an angle of 180 degrees, the two capillaries are alternately placed in the line. After sealing the flowmeter into the line, the manometer limbs are

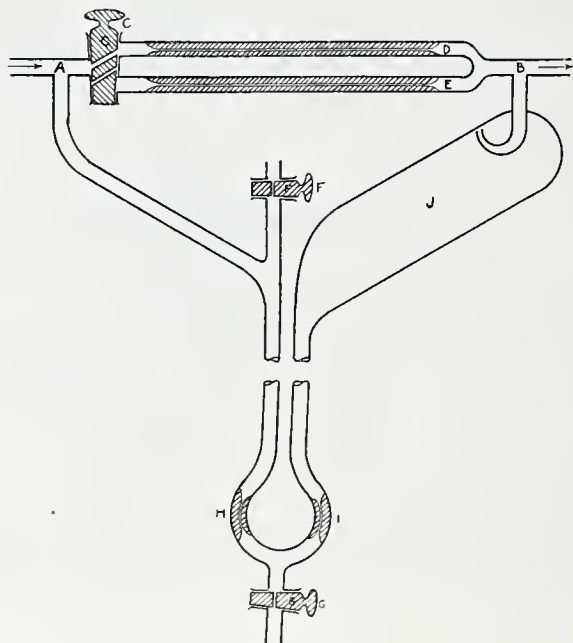


FIGURE 1

filled through stopcock *F*. If too much manometer liquid is allowed to flow in, or if it is necessary to change the liquid, it may be removed through stopcock *G*. *H* and *I* are constrictions which smooth out any pulsations in flow due to the passage of the gas through a wash liquid. The bulb *J* prevents the manometer liquid from being blown into the line because of a sudden rush of gas. The liquid is merely blown into the bulb and when conditions are normal again, it drains back into the limbs of the manometer.

If more than two ranges are desired, another ensemble of a three-way stopcock and two capillaries may be sealed on at *A* and *B*. Stopcock *C* is then turned through an angle of 90

degrees, closing off both *D* and *E*, and the new range may then be adjusted.

If a three-way stopcock is not available, the capillaries may be sealed on in parallel, using one ordinary two-way stopcock for each.

In Figure 2 the gas passes in at *A* and up into *C*, which is joined to the rest of the flowmeter by a ground-glass joint. The gas then goes down the capillary which is in mesh with *B* and out to the rest of the line. *C* is held to the rest of the apparatus by means of wire or small springs and the arms *M*, *O*, and *P*.

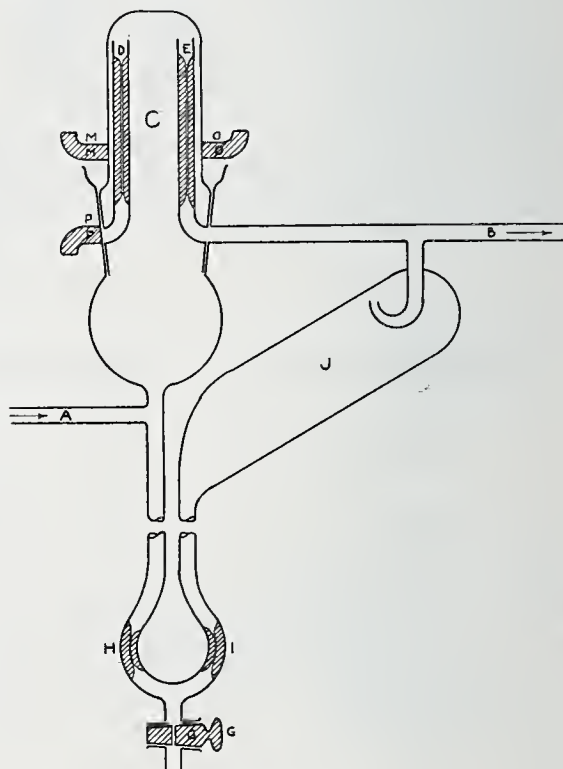


FIGURE 2

To change the range of this flowmeter, *C* is rotated through such an angle as to bring the proper capillary in mesh with *B*. Although only the two capillaries *D* and *E* are shown in the drawing, three or four may be sealed on, giving as many ranges. In filling the manometer arms, *C* is removed and the liquid introduced.

ACKNOWLEDGMENT

The writer wishes to acknowledge the helpful suggestions of A. Cameron in the design of these flowmeters.

RECEIVED January 4, 1932

A Double-Tube Combustion Furnace

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THE furnace here described was designed to shorten the time required for combustion analysis of organic compounds. It carries two tubes but permits the temperature of either to be regulated at will without affecting the other. This is accomplished by use of wide-topped burners mounted on a frame movable in any horizontal position, together with a flame spreader and a partition between the tube compartments. In addition to this principal feature, the furnace is lighter than the usual gas models, has no breakable clay tiles, and radiates less heat into the room with consequent economy of gas and increased comfort to the operator.

The end of this furnace is shown in Figure 1. Rivets are indicated by solid dots, and bolt holes by circles. The uprights *A* and the crosspieces *B* and *D* are made from 3.2 by 25.4 mm. (0.125 by 1 inch) iron bar, *C* of 3.2 by 50.8 mm. (0.125 by 2 inch), and *E* of 3.2 by 12.2 mm. (0.125 by 0.5 inch) stock. Pieces of transite board which line the heating chamber are shown by broken lines. Two of these are slotted to form sliding gates to permit easy removal of the combustion tubes. The ends are held together at *I I* by 12.2-mm. (0.5-inch) rods provided with nuts on each side of the upright. As in the Bunsen furnace, the upper rods support the tiles in the open position. The burner unit rests on *B* but is not fastened, and may be moved as desired. The modified V grooves, *F*, *G*, and *H*, carry angle irons which in the order named spread the flame, serve as troughs for the tubes, and support the sides and cover tiles. The end of each angle iron is cut away so it

will rest in the flattened notch with a shoulder indicated by the dotted lines at *F* which bears against the crosspiece and prevents the angle slipping out of position.

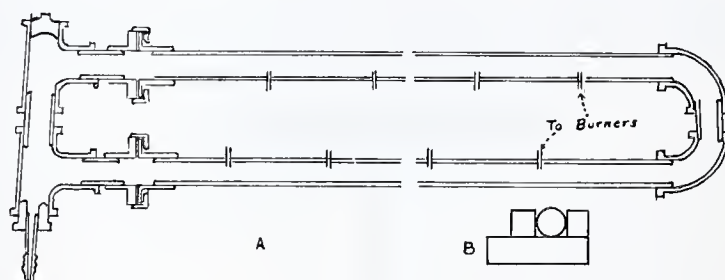


FIGURE 2. CONSTRUCTION OF BURNER ASSEMBLY

A, base; B, holder

Figure 2 shows the construction of the burner assembly. Twelve Fisher burners with bases tapped for screwing into pipelines are used. The pipe and fittings required are:

No.	DIMENSIONS
2	19.2 × 838 mm. (0.75 × 33 inch) extra heavy gas pipe
2	19.2-mm. (0.75-inch) ells
2	19.2 × 50.8 mm. (0.75 × 2 inch) nipples
2	19.2-mm. close nipples
2	19.2-mm. unions
2	19.2-mm. tees
1	19.2-mm. plug
1	19.2- to 9.6-mm. (0.75- to 0.375-inch) bushing
1	9.6-mm. (0.375-inch) hose connection to attach 8-mm. rubber tubing
12	3.2-mm. (0.125-inch) close nipples (brass)

¹ Present address, Iowa State College, Ames, Iowa.

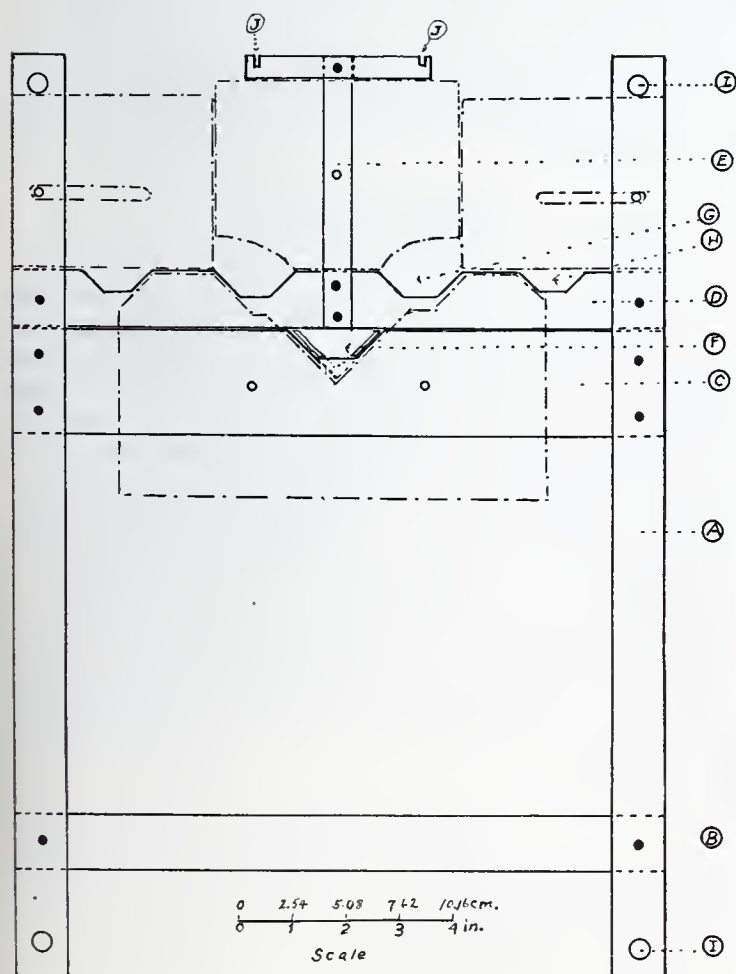


FIGURE 1. DIAGRAM OF END OF FURNACE

The construction of this unit is the most exacting operation in building the furnace, for the holes in the pipe must be in exact alignment so that the burner tops will be in a straight line. This was accomplished by use of a holder about a meter long made of three pieces of hardwood, as shown in Figure 2-B. The pipe is driven into this holder, and a straight line is marked on it by using the face of the holder as a guide for the scribe. The pipe is then turned so that the line is on top, and the positions of the holes are deeply punch-marked 11.43 cm. (4.5 inches) apart. A straight board is clamped to the drill table so that when the pipe holder is moved along against it



FIGURE 3. SECTIONAL VIEW OF TILE

the point of the drill is directly over the line. Small holes, 3.2 mm., are first drilled to serve as guides for the larger bit, 8.1 mm., which is the proper size for the tap. The holes are threaded by placing the tap in the drill chuck and turning it by hand. The pipe must not be moved in the holder at any time during the drilling and threading operations. The burners, which are not shown in the figure, must be taken apart for connection.

Metal-clad asbestos board is used for the top and sides instead of the usual clay tiles. A sectional view of one of these "tiles" is shown in Figure 3. The inner layer is of 6.4-mm. transite, the middle one of 6.4-mm. soft asbestos board, and the backing of 26-gage black sheet iron. This is superior to clay in insulating qualities and is practically unbreakable. A small eye bolt inserted through a hole near the top of each tile affords a convenient means for lifting it either with a wire hook or with tongs.

An end view of the top and the partition is shown in Figure 4. The top is made in the same manner as the tiles. It rests on 3.2 by 12.7 mm. bars set in the notches *J J* (Figure 1), and is held above these bars by transite blocks which thus provide a vent for hot gases from the burners. The partition is made of a single sheet of transite bound on the edges and held to the top by sheet-iron straps and stove bolts through the support blocks. The top and partition should be made in two sections, each half the length of the furnace, and all bolt holes should be appreciably larger than the bolts used to prevent warping and cracking of the asbestos. The iron bars which support the top extend about 40 cm. beyond the end of

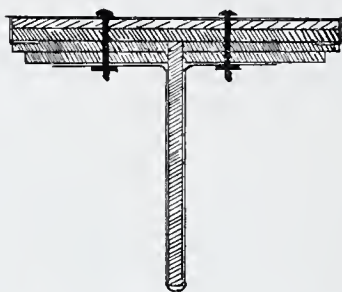


FIGURE 4. END VIEW OF TOP AND PARTITION

the furnace, so that absorption bulbs may be hung from them. The lower edge of the partition rests in the angle-iron flame spreader which is protected by transite strips held in place by metal straps.

A sectional view of the sides and bottom is given in Figure 5. The center piece *A* is drilled with 28.6-mm. holes, which fit the tops of the burners. A few of the burners are almost certain to be sufficiently out of line to hold it in place by friction. It is not fastened to the other part of the casing, but is movable with

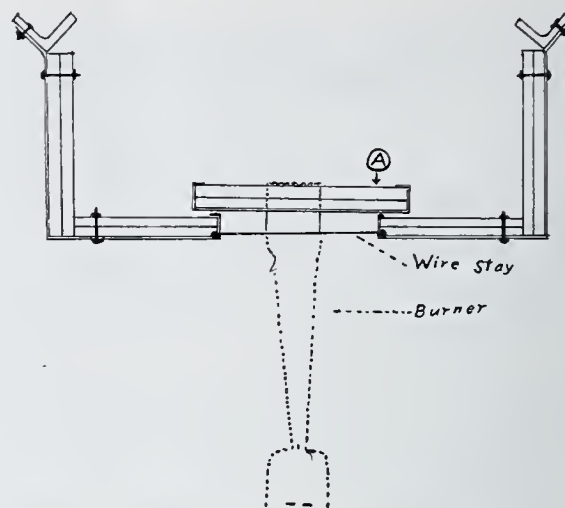


FIGURE 5. SECTIONAL VIEW OF SIDES AND BOTTOM

the burner rack. A transverse partition of transite on each side of the region near the boats aids regulation of temperature in this section. An extra tile of small size that fits between these partitions and rests against the flame spreader and the bottom of the furnace permits cutting the heat entirely off from under one boat while the rest of the tube and the entire length of the other are kept at maximum temperature. The burners may also be shifted so that they are entirely under one tube, or so that the flame is under only one tube at one end but divided between both at the other.

The furnace has proved entirely satisfactory on a series of test runs. The only defect noted was a tendency of the iron troughs and flame spreader to sag. This could evidently be corrected by making these parts of nickel.

RECEIVED July 17, 1931.

Determination of Mercury in Oil Preparations of Organo-Mercurials

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IN THE determination of mercury in medicinal preparations of organo-mercurials in oil, it is impracticable to attempt to destroy the organic matter (1) because of the relatively large sample which must be taken in order to have sufficient mercury for an accurate assay.

The following method is based on the ability of strong mineral acids to decompose many organo-mercurials to compounds which, when treated with hydrogen sulfide, give mercury sulfide (2).

The procedure was evolved for the assay of a preparation containing 0.040 per cent 4-nitroanhydrohydroxymercuri-*o*-cresol in mineral oil. It is presented in the hope that it may aid those who have similar preparations to assay. The method cannot be applied to those compounds whose mercury is not completely split off by concentrated hydrochloric acid.

A 100-gram sample is diluted with 100 cc. of petroleum ether, and 50 cc. of concentrated hydrochloric acid are added. The flask is placed in a shaking machine where it is shaken vigorously for 2 hours, or the contents may be stirred for the same length of time with a mechanical stirrer. The contents of the flask are transferred to a separatory funnel. The flask is rinsed with three 10-cc. portions of water and the rinsings added to the contents of the funnel. The acid layer is

drawn off through wet filter paper into the precipitation flask, the wet paper retaining any oil. The funnel and filter paper are washed with three 10-cc. portions of water and the washings are added to the contents of the precipitation flask. The solution is neutralized with gaseous ammonia, rendered acid with hydrochloric acid, and the mercury precipitated as mercury sulfide. The precipitate is transferred to a weighed Gooch crucible and washed with water, alcohol, carbon disulfide, and ether. It is dried at 100° C., cooled, and weighed as mercury sulfide.

Two 100-gram samples containing 0.04 gram each of 4-nitroanhydrohydroxymercuri-*o*-cresol analyzed by this method gave results from 1 to 3 per cent high.

Dyes do not interfere with the assay, which gives satisfactory results with solutions containing as little as 0.02 per cent mercury.

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Determination of Sulfur in Coal by Perchloric Acid Method

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THE Eschka bomb-washing and sodium peroxide methods are commonly employed in the determination of sulfur in coal. Check determinations of sulfur in coal and coke were carried out using samples from various sources of supply throughout the United States by committee D-5 of the American Society for Testing Materials, and the results published by Selvig and Fieldner (1). Sixteen samples were studied by various testing laboratories and corporations, and by the Bureau of Mines. The results reported showed a wide enough variation between methods and operators to justify the study of a new method for this determination. Both the bomb-washing method and the sodium peroxide-fusion method are in use as substitutes for the Eschka method because of their speed. The perchloric acid method, like the latter two named above, is fast and has the added advantage that it requires no special apparatus such as a bomb or muffle furnace. Since a similar successful method has been developed for the determination of sulfur in rubber using perchloric acid, by Wolesensky (3), it was thought worth while to extend the application with necessary modifications to the analysis of coal.

GENERAL CONSIDERATIONS

The general subject of the oxidation of coal using perchloric acid was studied under the following headings:

FACTORS AFFECTING OXIDATION OF ORGANIC MATTER

1. Acid strength
2. Temperature of reaction
3. Influence of catalysts
4. Influence of highly volatile combustible matter
5. Use of monochloroacetic acid to prevent frothing during digestion of sample

FACTORS AFFECTING OXIDATION OF SULFUR

1. Partial oxidation of sulfur by perchloric acid
2. Complete oxidation of sulfur using nitric acid plus potassium nitrate
3. Effect of catalyst on precipitation of barium sulfate

These factors will, therefore, be discussed in the order given.

INFLUENCE OF STRENGTH AND TEMPERATURE OF PERCHLORIC ACID. Over the temperature range of 180° to 200° C. 70 per cent perchloric acid completely oxidized equal portions of the same sample of a given coal or coke at a rate roughly twice as fast for each increase of 10° in temperature. The average sample of coke requires 9 hours at approximately 200° C. for complete oxidation. The average sample of coal requires 3 hours for complete oxidation under similar conditions. Increasing the concentration of perchloric acid from 70 to 73 per cent divides the time interval required for complete oxidation roughly by three. The time required even when using the 73 per cent perchloric acid is thus seen to be excessive. A study was made, therefore, to select a suitable catalyst for the reaction.

SELECTION OF CATALYST. From an extensive list of

A solution and digestion method for the oxidation of coal using strong perchloric acid preparatory to the determination of sulfur by precipitation as barium sulfate is described, and the influence of several catalysts for use in shortening the time necessary for the destruction of organic matter in the presence of hot 70 per cent perchloric acid shown.

The advantages of this new method consist mainly in a saving of time with simultaneous elimination of the need for special equipment. The former advantage has previously been gained with the sacrifice of the latter. The method was examined by the analysis of six samples of coal with thirty individual determinations and the results compared with the Eschka method.

catalysts, the most satisfactory were cerium nitrate, chromic acid, and vanadic acid. Cerium nitrate was found to be effective to a small extent, but was erratic and sometimes caused a violent reaction. Hot concentrated perchloric acid oxidizes chromic and vanadyl salts to chromic and vanadic acid. Both of the latter substances are in turn reduced to lower stages of valence by the organic matter in the coal and reoxidized by the perchloric acid until the oxidation of the coal is complete. Vanadium added in the form of ammonium vanadate proved to be the most satisfactory. A sample of

coke requiring 9 hours for oxidation with 70 per cent perchloric acid at approximately 200° C., without a catalyst, could be completely oxidized in approximately 70 minutes using chromium and in approximately 10 minutes using vanadium as a catalyst. The increase in the velocity of the reaction with increase in concentration of the catalyst added is shown in Figure 1.

PREVENTION OF FROTHING AND RETARDATION OF OXIDATION PERIOD. Samples of coal with volatile matter higher than 35 per cent often catch fire when boiled with 70 per cent perchloric acid and, also, coal samples often froth excessively during the early oxidation period. Both of these difficulties were overcome by the use of from 2 to 4 grams of monochloroacetic acid. This reagent is slowly volatilized before the oxidation period is complete.

FACTORS INFLUENCING OXIDATION OF LOWER VALENCE SULFUR TO SULFURIC ACID. Hot concentrated perchloric acid only partially oxidizes the element sulfur to sulfuric acid. Volatile compounds of sulfur, oxygen, and chlorine, yet unidentified, are formed. Sulfur present in the coal in a form other than the sulfate would not be expected to oxidize to sulfuric acid, using perchloric acid alone as an oxidizing agent. This was found to be true, and nitric acid or potassium nitrate or a mixture of both was added to bring about the oxidation of the lower valence sulfur compounds to sulfuric acid. The addition of both monochloroacetic acid to prevent frothing and nitric acid to oxidize sulfur completely lowered the boiling point of the mixture but did not add appreciably to the oxidation period for any given coal (15 to 40 minutes).

The presence of chromium in the form of a chromic salt or as chromic acid and the presence of vanadic acid would be expected to result in their occlusion by the precipitated barium sulfate. With ammonium vanadate as catalyst this difficulty is eliminated by reducing the vanadium to a vanadyl salt by use of a small excess of hydroxylamine hydrochloride. Test precipitations of barium sulfate from perchloric acid solution in the presence of a chromate or vanadate did not result in appreciable occlusions, as shown by qualitative examination. The vanadium used as catalyst was always

reduced to a vanadyl salt by addition of hydroxylamine hydrochloride before the sulfuric acid was precipitated. The influence of the presence of perchloric acid on this precipitation has been described by Wolesensky (5). Unlike hydrochloric acid, perchloric acid may be present in considerable quantities without appreciable effect.

OUTLINE OF ANALYTICAL METHOD

Place accurately weighed gram samples of the coal in 300-cc. Erlenmeyer flasks together with a gram of potassium nitrate, 5 cc. of concentrated nitric acid, and 0.16 gram of ammonium vanadate. Add also 2 to 4 grams of monochloroacetic acid and 15 cc. of 70 per cent perchloric acid. Place the flask and contents on the hot plate at 120° C. with the flask uncovered. Digest for 10 minutes, and then heat on the hot

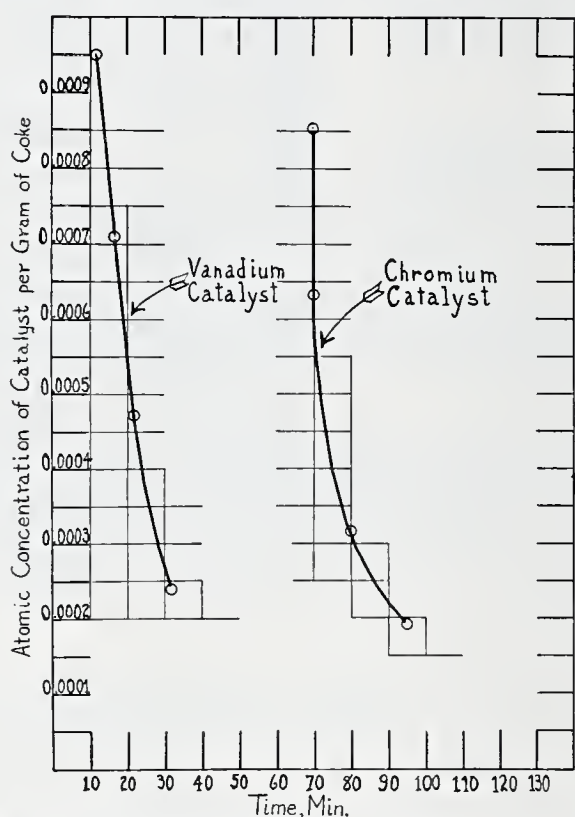


FIGURE 1. INFLUENCE OF VANADIUM AND CHROMIUM AS CATALYSTS IN OXIDATION OF COKE

plate at 180° to 185° C. until the coal is oxidized and an orange-red precipitate of vanadium pentoxide appears. This requires an additional 5 to 25 minutes, depending upon the nature of the coal, but is generally less than 10 minutes.

Remove the sample from the hot plate, cool somewhat, and add 5 to 10 cc. of concentrated hydrochloric acid. Return to the hot plate and heat until the orange-red precipitate of vanadium is again obtained. The addition of the hydrochloric acid speeds the removal of the nitric acid which is difficult to evaporate away, especially if the necessary digestion period for the oxidation of the sample is short. Remove the sample at this point from the hot plate and add 100 cc. of water and 0.2 gram of hydroxylamine hydrochloride. Heat to reduce the vanadic acid to vanadyl salt, filter insoluble matter, including the dehydrated silica of the sample (hot concentrated perchloric acid completely dehydrates silica, 2), and dilute the filtrate and washings with water to a 400 cc. volume. Heat to boiling and precipitate with barium chloride in the usual manner. Typical results are found in Table I.

The first three analyses of Table I (sample 40280) show the effect of omitting potassium nitrate or nitric acid to ensure complete oxidation of sulfur to sulfuric acid. The oxidation of sulfur by hot perchloric acid is not complete even though the oxidation period is extended for more than twice the

period required to oxidize the sample completely to the production of vanadic acid. The addition of 0.5 gram of potassium nitrate indicates the need for more potassium nitrate, or, in its place, nitric acid.

Analyses 4 to 9, inclusive (sample 40236), show the improvement in results by adding 1.0 gram of potassium nitrate or 5 cc. of concentrated nitric acid, with the greatest improvement effected by the use of 1.5 grams of potassium nitrate in the absence of nitric acid and a longer digestion period. These results indicate a preference in the use of both potassium nitrate and nitric acid to ensure complete oxidation of sulfur.

Analyses 10 to 14, inclusive (sample 40391), show the effect of the applications of the principles suggested in the preceding paragraph. The results obtained are persistently less than those obtained by the Eschka method, but are very concordant in duplicate determinations. The time of digestion in this case was purposely extended beyond that required for complete oxidation of the coal, as was likewise the time of the remaining analyses, for the reason given in the subsequent discussion.

Analyses 15 to 22, inclusive (samples 40300, 40438, and 40210), further parallel the conclusions of the above paragraph on three additional samples of coal. The analyses by the Eschka method (determinations 1 to 22, inclusive, Table I) were carried out at the Bureau of Mines Experiment Station, Pittsburgh, who kindly furnished samples for this investigation. The sulfur determination was calculated on the basis of the air-dry weight following the usual treatment.

TABLE I. COMPARISON OF ESCHKA AND PERCHLORIC ACID METHODS

ANALYSIS	COAL No.	HClO ₄		HNO ₃		MONO-CHLORO-ACETIC ACID		TIME OF REACTION, Min.	SULFUR		
		70% Cc.	KNO ₃ Grams	68% Cc.	KNO ₃ Grams	37% Cc.	HCl 37% Cc.		Present %	Eschka %	Diff. %
1	40280	15	None	None	None	None	None	15	4.32	2.56	-1.76
2	40280	15	None	None	None	None	None	35	4.32	3.12	-1.20
3	40280	15	0.5	None	None	None	None	20	4.32	4.04	-0.28
4	40236	15	1.0	None	3.0	None	None	30	3.14	2.98	-0.16
5	40236	15	1.0	None	3.0	None	None	30	3.14	2.98	-0.16
6	40236	10	None	5.0	2.0	None	None	30	3.14	3.08	-0.06
7	40236	10	None	5.0	2.0	None	None	30	3.14	3.07	-0.07
8	40236	15	1.5	None	3.0	10	None	45	3.14	3.12	-0.02
9	40236	15	1.5	None	3.0	10	None	45	3.14	3.17	+0.03
10	40391	15	None	5.0	3.0	10	None	35	6.11	5.85	-0.26
11	40391	15	None	5.0	3.0	10	None	35	6.11	5.86	-0.25
12	40391	15	1.0	None	4.0	10	None	55	6.11	5.84	-0.27
13	40391	15	1.0	None	4.0	10	None	55	6.11	5.98	-0.13
14	40391	15	1.0	5.0	3.0	10	None	50	6.11	5.81	-0.30
15	40300	15	1.5	None	3.0	10	None	45	1.58	1.52	-0.06
16	40300	15	1.5	None	3.0	10	None	45	1.58	1.50	-0.08
17	40438	15	1.5	None	3.0	4	None	45	2.07	1.94	-0.13
18	40438	15	1.5	None	3.0	4	None	45	2.07	1.94	-0.13
19	40210	15	1.0	None	3.0	5	None	45	1.06	0.97	-0.09
20	40210	15	1.0	None	3.0	5	None	45	1.06	0.96	-0.10
21	40210	15	None	5.0	5.0	None	None	100	1.06	0.99	-0.07
22	40210	15	None	5.0	5.0	None	None	100	1.06	0.97	-0.09
23	40212	15	None	5.0	3.0	10	None	35	3.50	3.58	+0.08
24	40212	15	None	5.0	3.0	10	None	35	3.50	3.59	+0.09
25	40224	15	None	5.0	3.0	10	None	120	2.17	2.13	-0.04
26	40224	15	None	5.0	3.0	10	None	120	2.17	2.12	-0.05
27	40224	15	None	5.0	3.0	10	None	50	2.17	2.16	-0.01
28	40224	12	None	5.0	3.0	10	None	50	2.17	2.12	-0.05
29	40224	12	None	5.0	3.0	10	None	60	2.17	2.12	-0.05

Samples 12 and 24 were supplied through the courtesy of the analytical division of the University of Michigan and were of the type having high volatile matter (approximately 45 per cent). The agreement between the results for the perchloric acid method and the Eschka method are more satisfactory in these cases.

In many cases (for example, samples 40210 and 40224) the time of digestion of the coal was purposely greatly extended over that necessary for complete oxidation. The average time required for the oxidation of the organic matter fell in the range 5 to 30 minutes, or approximately 15 minutes, for all samples of Table I. The preliminary digestion period of 10 minutes at a temperature of 120° C. is advisable if the volatile

matter in the coal is not known to be less than 35 per cent. Longer periods of digestion (60 to 120 minutes) were employed in search of results indicating the loss of sulfuric acid by volatilization. This might be expected but was not found at the temperatures of the boiling 70 per cent perchloric acid (200° C.) under ordinary barometric pressures. (Compare analyses 21 and 22 with 19 and 20, as well as analyses 25 and 26 with 27 and 28.)

COMPARISON OF ESCHKA AND PERCHLORIC ACID METHODS

A comparison of the Eschka and perchloric acid methods for the determination of sulfur in coal is hardly justified on the basis of the present work when compared with the work of Selvig and Fieldner (1). The results as reported in this paper are distinctly low in tendency as compared to the Eschka method. This may be in part due to two influences: First, by digestion with perchloric acid, the silica of the coal is dehydrated and completely removed with the small amount of insoluble matter before barium sulfate is precipitated. This probably is a much more complete removal of silica from the solution before barium sulfate is precipitated than by all the methods investigated by Selvig and Fieldner. Second, because of a comparatively high concentration of perchloric acid at the time of precipitation of barium sulfate in the

method of this paper, complete precipitation of the barium sulfate does not result (3). This error is not alone sufficient to account, except in part, for the low results obtained.

APPLICATION OF METHOD TO ANALYSIS OF COKE

The method as described was applied to the analysis of coke and gave very satisfactory comparisons in values obtained for some samples and very poor results for others. The discrepancies were not explained, and, until this can be done and the remedy found, the method is not recommended for sulfur determinations in coke.

ACKNOWLEDGMENT

Appreciation is expressed for the coöperation of the U. S. Bureau of Mines at Pittsburgh and to H. H. Willard of the University of Michigan for supplying samples with analyses to be used in this investigation.

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Carbonate Content of Volumetric Sodium Hydroxide Solutions

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THE best reagent quality of sodium hydroxide contains more than 1 per cent of sodium carbonate. Various methods have been devised for removing carbonate from sodium hydroxide solutions intended for volumetric analysis. These methods include (1) precipitation with the hydroxides or soluble salts of the alkaline earths; (2) utilizing the small solubility of sodium carbonate in a concentrated solution of sodium hydroxide which is known as "oil lye" (14); (3) using metallic sodium with ether vapor as a barrier against atmospheric carbon dioxide (3); and (4) employing an electrolytically prepared sodium amalgam (1, 5).

For general use, the precipitation and oil lye methods are preferred for their simplicity and the ease with which large quantities of solution can be prepared. The authors determined the small amounts of sodium carbonate remaining in such solutions prepared under practical conditions, by both gravimetric and volumetric methods.

PREPARATION OF VOLUMETRIC SODIUM HYDROXIDE SOLUTIONS

Carbon dioxide-free water was used in all the experiments. The methods used for removing carbon dioxide from water, for storing and standardizing volumetric solutions, and for filling burets were the same as those described by Han and Chu (4). The sodium hydroxide was of reagent quality (Merck's pure), and a sample of it was found to contain 1.40 per cent of sodium carbonate. All sodium hydroxide solu-

The minute amount of carbonate present in "oil lye" and sodium hydroxide solutions treated with various precipitants has been determined by gravimetric and volumetric methods. Barium hydroxide and salts were found to be the most effective precipitants. The technic of Warder's method of differential titration has been improved and the results obtained checked within 0.02 per cent against the gravimetric evolution method.

tions were filtered through Jena sintered-glass crucibles, G4 (7). Filtration and siphoning were carried out in absence of carbon dioxide.

MILK OF LIME (6) AND CALCIUM CHLORIDE METHODS. One hundred twenty-five grams of sodium hydroxide were dissolved in water and made up to 2.7 liters. To this 300 cc. of milk of lime, prepared from 20 grams of mar-

ble lime, or 300 cc. of a solution containing 16 grams of calcium chloride (dry neutral granules, Merck's reagent) were added. The mixture was vigorously shaken for an hour and allowed to settle for at least 4 days.

OIL LYE METHOD (14). Five hundred grams of sodium hydroxide were dissolved in 500 cc. of water in a stoppered measuring cylinder of Jena glass. The total volume amounted to about 645 cc. A rubber stopper carrying a soda lime tube and a siphon was fitted into the neck of the cylinder. The lye was clarified by heating near the boiling point of water (10) in a specially constructed water bath for several hours, and cooled slowly. The water bath was provided with a false bottom and the measuring cylinder was completely enclosed except for the neck.

For a normal solution, about 240 cc. of the oil lye from the center of the container and sufficient water for diluting to 4.5 liters were siphoned into a 5-liter bottle without access of carbon dioxide, and mixed.

METHODS USING HYDROXIDES OR SALTS OF STRONTIUM AND BARIUM AS PRECIPITANTS. For a 4 N stock solution (13), 170 grams of sodium hydroxide were dissolved in water and

TABLE I. COMPARISON OF GRAVIMETRIC AND VOLUMETRIC METHODS

VOLUMETRIC NaOH SOLN. USED	GRAVIMETRIC METHOD		VOLUMETRIC METHOD							
	Soln. No. ^a	Normality	Carbonate in total alkali %	Soln. No. ^a	Normality	ACID INTO ALKALI		Devn. from grav. method	ALKALI INTO ACID Carbonate in total alkali %	Devn. from grav. method
						Carbonate in Total Alkali	Cor. ^b			
						Obsvd. %	%			
Ca(OH) ₂ siphoned	1	1.155	1.03	1	1.155	1.07	1.04	+0.01	0.56	-0.37
			1.04			1.07	1.04		0.66	
			1.03			1.07	1.04		0.76	
			1.03			1.07	1.04		0.66	
Ca(OH) ₂ siphoned	2	1.024	1.09	2	1.024	1.12	1.09	+0.01	0.48	-0.50
			1.07			1.12	1.09		0.60	
			1.08			1.11	1.08		0.65	
			1.08			1.12	1.09		0.58	
CaCl ₂ siphoned	3	0.9388	1.07	3	0.9388	1.09	1.06	0.00		
			1.06			1.09	1.06			
			1.06			1.08	1.05			
			1.06			1.09	1.06			
Oil lye siphoned ^c	4	1.058	0.15	4	1.058	0.19	0.16	+0.01	0.11	-0.04
			0.12			0.18	0.15		0.10	
			0.15			0.18	0.15		0.10	
			0.14			0.18	0.15		0.10	
Oil lye filtered ^c	5	1.043	0.13	5	1.043	0.18	0.15	+0.02	0.11	-0.01
			0.13			0.19	0.16		0.11	
			0.14			0.18	0.15		0.14	
			0.13			0.18	0.15		0.12	
Sr(OH) ₂	6a	4.091	0.06	6b	1.114	0.08	0.06	0.00		
			0.06			0.08	0.06			
			0.06			0.08	0.06			
			0.06			0.08	0.06			
SrCl ₂ siphoned	9a	4.010	0.02	9b	0.8020	0.04	0.02	0.00		
			0.02			0.04	0.02			
			0.02			0.04	0.02			
			0.02			0.04	0.02			
Ba(OH) ₂ filtered	13a	4.103	0.01	13b	0.9965	0.03	0.01	0.00		
			0.01			0.04	0.02			
			0.01			0.03	0.01			
			0.01			0.03	0.01			
BaCl ₂ siphoned	15a	4.305	0.01	15b	0.9493	0.04	0.02	+0.01		
			0.01			0.04	0.02			
			0.01			0.03	0.01			
			0.01			0.04	0.02			
BaCl ₂ + Ba(OH) ₂ siphoned	19a	3.756	0.01	19b	0.9109	0.03	0.01	+0.01	0.03	+0.01
			0.01			0.04	0.02		0.02	
			0.01			0.04	0.02		0.01	
			0.01			0.04	0.02		0.02	

^a Solution "b" was prepared by diluting solution "a" of the same number.
^b For percentages above 0.10, correction is 0.03; for lower percentages, only 0.02.
^c Solutions 4 and 5 were prepared from same oil lye.

mixed with a solution of the precipitant. The solution was diluted to 1 liter and allowed to settle overnight.

For a normal solution, 750 cc. of the clear stock solution were siphoned into a 4-liter flask and diluted to 3 liters. The solutions remained clear after dilution with an excess of precipitant present.

For 1 liter of a 4 N solution, the following quantities of precipitants were used: Sr(OH)₂·8H₂O, 9.8 grams; SrCl₂·6H₂O, 9.8 grams; Sr(NO₃)₂, 7.8 grams; Ba(OH)₂·8H₂O, 11.6 grams; BaCl₂·2H₂O, 9 grams; Ba(NO₃)₂, 9.6 grams. Strontium hydroxide was dissolved in boiling water, added to the sodium hydroxide solution, and the mixture shaken for some time.

BARIUM NITRATE AND SODIUM SULFATE METHOD. The details were the same as those described by Han and Chu (4).

BARIUM CHLORIDE AND BARIUM HYDROXIDE METHOD (8). A normal sodium hydroxide solution previously treated with barium chloride and freed from barium carbonate was nearly saturated with barium hydroxide.

GRAVIMETRIC ESTIMATION

The apparatus used was an ordinary carbon dioxide train. The carbon dioxide liberated passed successively through concentrated sulfuric acid and phosphoric anhydride, and was absorbed in a Fleming bulb containing soda lime and phosphoric anhydride. Sulfuric acid was used for acidifying the sample. Where the sample was treated with a chloride in its preparation, a saturated solution of silver sulfate in 18 N sulfuric acid was used for removing the traces of hydrogen chloride that happened to pass over. The air used for sweep-

ing the train was thoroughly washed by passing successively through two spiral wash bottles containing 28 per cent potassium hydroxide solution (16).

VOLUMETRIC ESTIMATION

Although accurate and reliable, the gravimetric method requires 200 to 700 cc. of sample and considerable time for each determination. A quick volumetric method is desirable, using 45 cc. of sample and giving results of comparable accuracy.

For the volumetric analysis of hydroxide-carbonate mixtures, the method of Winkler is usually used. However, for the minute amount of carbonate left in a solution of sodium hydroxide after treatment with barium salt, this method is not suitable.

Warder's method (15) is generally considered as being less accurate. Loss of carbon dioxide before the first end point and the hydrolysis of bicarbonate are the usual causes of error. Fortunately no difficulty is encountered when the amount of carbonate is small. The result for carbonate is seriously affected, however, by slight errors in the two end points. Thus, if 45 cc. of standard acid are used for the complete titration, and an error of 0.04 cc. of acid is made in each end point, the result for carbonate would be affected by 0.35 per cent when the errors are accumulative in nature. Rather (11) modified the original procedure of Warder by titrating nearly to the first end point with 2 N acid and finishing both with 0.2 N acid. With this method of decimal end-point titration and other refinements in technic, the authors have been able to improve the precision to a remarkable degree. The results

obtained, after correction, checked the gravimetric method within 0.02 per cent.

APPARATUS. A 50-cc. stopcock buret with a long nozzle was used for *N* hydrochloric acid. The nozzle was inserted through the central hole of a three-holed rubber stopper, whose two side holes carried a bent glass tube and a soda lime tube. During titration, the stopper was fitted into a 200-cc. Erlenmeyer flask of Jena glass, and a current of carbon dioxide-free air was passed into it through the bent glass tube without bubbling through the solution. The Erlenmeyer flask was thoroughly rinsed with carbon dioxide-free water immediately before use. The buret was flexibly supported from above, so that the Erlenmeyer flask could be rotated during titration. All burets were protected with soda lime tubes.

MATERIALS. Hydrochloric acid, 1 *N* and 0.01 *N*: The normal solution was freed from carbon dioxide by boiling for 20 minutes and standardized against sodium carbonate. The 0.01 *N* solution was prepared by diluting the normal solution with carbon dioxide-free water.

Sodium hydroxide, 0.01 *N*: A measured amount of oil lye was diluted and standardized against the 0.01 *N* hydrochloric acid.

PROCEDURE. A plug of cotton wool was inserted into the neck of a 200-cc. Erlenmeyer flask, and carbon dioxide-free air was passed through it, until the end of the analysis. Then 45 cc. of the 1 *N* sodium hydroxide solution to be analyzed were introduced from a long-nozzle buret without removing the cotton plug. Two drops of phenolphthalein were added. The three-holed rubber stopper was immediately fitted into the flask, and 1 *N* hydrochloric acid, about 0.05 cc. less than that required for complete neutralization, was added very slowly. (The exact amount for complete neutralization was determined by a preliminary titration.) During the addition of acid, the flask was gently rotated to effect thorough mixing of its contents. The three-holed rubber stopper was removed from the flask and 0.01 *N* hydrochloric acid added until the faint pink color was just discharged as shown by comparison with water in a similar flask. A known amount of 0.01 *N* hydrochloric acid was added and the solution boiled for 15 minutes under a small reflux condenser with a current of carbon dioxide-free air slowly bubbling through it. A soda lime tube was fitted into the flask and the solution cooled with running water. The excess acid was titrated back with 0.01 *N* sodium hydroxide, and the faint pink color was finally discharged again with 0.01 *N* acid.

The first end point was sharper when only small quantities of carbonate were present.

The results obtained were expressed in terms of total alkali. Thus if 45 cc. of normal acid were used for the complete titration and 2.25 cc. of 0.01 *N* acid used for the second end point, then 0.10 per cent of the total alkali present was in the form of carbonate.

COMPARISON OF RESULTS. Table I gives a comparison of the results by the two methods. The volumetric method gave slightly higher results than the gravimetric and the difference increased with the carbonate content of the sodium hydroxide solution. For percentages lower than 0.1, the correction was about 0.02, while for higher percentages of carbonate, it amounted to 0.03. Other results obtained by the volumetric method are shown in Table II.

The volumetric method is suitable for estimating the carbonate content of volumetric sodium hydroxide solutions, although with less than 0.03 per cent the accuracy is rather uncertain.

REVERSED TITRATION. Unreliable results are obtained if alkali is run into acid during the titration.

TABLE II. VOLUMETRIC ESTIMATIONS

SOLN. No.	NaOH SOLN. USED	NORMALITY	CARBONATE IN TOTAL ALKALI ^a
			%
1	Ca(OH) ₂	1.155	(1.04)
2	Ca(OH) ₂	1.024	(1.09)
3	CaCl ₂	0.9388	(1.06)
4	Oil lye	1.058	(0.15)
5	Oil lye	1.043	(0.15)
6b	Sr(OH) ₂	1.114	(0.06)
7	Sr(OH) ₂ filtered	1.049	0.04 0.04 0.04 (0.02)
8	Sr(OH) ₂ siphoned	1.116	0.03 0.03 0.04 (0.01)
9b	SrCl ₂	0.8020	(0.02)
10	SrCl ₂ filtered	0.9955	0.05 0.04 0.04 (0.02)
11	Sr(NO ₃) ₂ siphoned	0.9834	0.04 0.04 0.04 (0.02)
12	Sr(NO ₃) ₂ siphoned	1.062	0.04 0.04 0.04 (0.02)
13b	Ba(OH) ₂ filtered	0.9965	0.03 0.04 0.03 (0.01)
14	Ba(OH) ₂ filtered	0.9457	0.04 0.04 0.04 (0.02)
15b	BaCl ₂	0.9493	(0.02)
16	BaCl ₂ siphoned	1.020	0.04 0.04 0.03 (0.02)
17	Ba(NO ₃) ₂ siphoned	0.9434	0.02 0.02 0.03 (0.00)
18	Ba(NO ₃) ₂ siphoned	1.089	0.02 0.03 0.03 (0.01)
19b	BaCl ₂ + Ba(OH) ₂	0.9109	(0.02)
20	BaCl ₂ + Ba(OH) ₂ filtered	1.092	0.03 0.03 0.04 (0.01)
21	Ba(NO ₃) ₂ + Na ₂ SO ₄ siphoned	1.090	0.01 0.01 0.02 (0.00)
22	Ba(NO ₃) ₂ + Na ₂ SO ₄ (BaCO ₃ filtered, BaSO ₄ siphoned)	0.9803	0.02 0.02 0.02 (0.00)
23	Ba(NO ₃) ₂ + Na ₂ SO ₄ siphoned	0.8845	0.02 0.03 0.03 (0.01)

^a Figures in parentheses are corrected average values.

COMPLETENESS OF CARBONATE REMOVAL

The authors did not attempt to make a study of solubilities. The results presented show only the carbonate content of sodium hydroxide solutions treated and tested under practical conditions.

Barium hydroxide and salts remove carbonate most completely and are to be recommended for general use. Although strontium carbonate is less soluble than barium carbonate (9), yet strontium compounds were found to be less reliable for carbonate removal. Milk of lime does not remove carbonate so completely as compounds of strontium or barium, but

it has the decided advantage of introducing the least amount of alkaline earth into the solution.

The oil lye method has the advantage of requiring no precipitant. In a number of normal solutions prepared, 0.09 to 0.18 per cent of the total alkali was found to be present in the carbonate form, corresponding to 0.0048 to 0.0095 gram of actual sodium carbonate per 100 cc. Coles (2) obtained a 0.1 *N* solution of sodium hydroxide which gave no precipitate with barium hydroxide, by settling oil lye overnight and diluting a portion with freshly boiled water. Rising (12) prepared a similar 0.1 *N* solution by filtering oil lye and diluting with water which had been re-distilled over barium hydroxide, and found that the sodium carbonate content was about 0.0005 per cent.

ACKNOWLEDGMENT

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Composition of Vapors from Boiling Binary Solutions

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A PREVIOUS article (2) described a method and apparatus having several advantages for the determination of the composition of vapors arising from boiling solutions of two volatile liquids. Since this work was published, this system has been used by the writer and others in obtaining data necessary for several types of engineering problems, and various improvements have been made in the design of the glass apparatus.

APPARATUS USED

Figures 1 and 2 illustrate the apparatus¹ used more recently in studies of this nature. It is constructed of Pyrex glass, and it will be seen that, although several changes have been made, the same principles which governed the design previously used have been followed. An internal electric heater, incorporated in the Kjeldahl flask which serves as the boiling pot, is the largest single change, although the improved unit without the electric heater has been used as before, giving excellent results with an external electric heater or a Bunsen flame.

The unit is fabricated in one piece, being built around a standard Kjeldahl flask. This design is much simpler in construction, and offers several other advantages over the previous one which used a length of large-diameter glass tubing. The methods and details of construction are apparent by reference to the figures, and the changes from the earlier model may be noted by comparison with the figure in the previous article. If an external heat source is to be used rather than the internal one shown, the drain tube for sampling the boiling liquid is attached to the bottom of the flask at a point opposite the inlet from the condensate reservoir, and supplied with a cock as before.

¹ The writer is prepared to supply direct orders for this apparatus.

Vapor-composition curves, elevation of boiling points of solutions, and related data on liquid-vapor systems necessary for the design of engineering equipment may be obtained conveniently and accurately with the apparatus and method described. This work is an improvement over that previously published which has been used by several others also, in obtaining various data. Several representative vapor-composition curves are given.

The heating unit is formed by itself before attachment to the rest of the unit. It should be designed to draw between 100 and 200 watts of power. Platinum and nichrome coils have been used, and tungsten² would be useful because of its low coefficient of thermal expansion which approximates that of Pyrex, in making seals. Because of the high resistance of nichrome, a heater of this metal may be designed to

operate across an ordinary 110-volt circuit, but a platinum-coil unit should be designed to operate at a reduced voltage. The calculated length of wire is wound on a tube of Pyrex previously pierced with two very small holes at each end of the length reserved for the coil. The ends of the wire terminate in mercury wells attached to the sides for connection to the power supply. The lower end of the tube carrying the heating coil is pierced with four holes about 5 mm. in diameter as close as possible to the inseal, so that no pocket is formed for liquid to remain undisturbed during the operation.

OPERATION. When the flask is charged and current supplied, the bare wires lose their heat very readily to the surrounding liquid. The vapor bubbles cause the boiling liquid to rise around the coil, drawing fresh liquid down through the tube, and through the holes at the bottom. A cycle is made which ensures complete mixing throughout the liquid phase. Because of the very small bubbles formed in contact with the fine wire, which is at a temperature only slightly above the boiling point of the solution, and the homogeneity of this solution, this boiling is probably very nearly an "equilibrium vaporization."

Vapor compositions have been determined from pressures

² Tungsten wire may now be obtained from the Fansteel Co., Chicago, Ill.



FIGURE 1. APPARATUS FOR DETERMINING VAPOR COMPOSITION

a few centimeters of mercury above atmospheric down to low pressures comparable to those employed industrially for vacuum distillation. For pressures above the barometer, the vent is connected to the manometer of the constant-pressure controller previously described (4) and the operation is followed the same as at atmospheric pressure. For vacuum runs, the vent from the vapor jacket and the vent from the condensate reservoir are connected to a 12-liter Pyrex glass flask for a capacity effect, a vacuum pump, and a manometer. The vacuum connection to the vapor jacket has a cock which is closed when the system is purged of air. The manometer has an electrical contact which breaks when the vacuum exceeds the set point and releases a solenoid operating a vacuum leak.

As mentioned above, the apparatus shown in Fig-

ure 1, but without the electrical heating unit sealed to the bottom of the flask, has been used with an external source of heat. This type of unit is simpler in construction and has all of the advantages of the other, except those due to the peculiar type of boiling which the internal electrical heater causes. The method of operation for determining x, y curves is exactly the same as previously described, and the same advantages which were previously noted may be expected to an accentuated degree of the modified apparatus.

TABLE I. RESULTS WITH APPARATUS OF USUAL TYPES OF BINARY VAPOR COMPOSITION CURVES

BENZENE-ACETIC ACID (% BENZENE)		WATER-FORMIC ACID (% WATER)		ACETIC ACID-ACETIC ANHYDRIDE (% ACETIC ACID)	
Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
Wt. %	Wt. %	Wt. %	Wt. %	Wt. %	Wt. %
91	94.60	10	6.0	10	23.2
92	94.95	20	18.2	20	42.3
93	95.30	23.5	23.5	30	56.5
94	95.90	30	34.8	40	65.2
95	96.40	40	50.2	50	72.4
96	96.95	50	64.4	60	78.6
97	97.50	60	75.8	70	84.1
98	98.10	70	83.6	80	89.7
98.5	98.50	80	90.2	90	95.0
99	98.85	90	95.8		
99.5	99.25				

ADVANTAGES. The new apparatus has the following differences:

1. Simpler in design and construction, a standard size flask substituted for the large glass tubing. Smaller, more compact, less fragile.
2. Greater ease of insulating vapor jacket if desirable (2).
3. Free end on vapor tube leaving flask ground to wedge shape. This allows insertion of the thermometer bulb directly in the liquid if desired. The tip previously used is excellent for preventing priming where a countercurrent of liquid passes against a rising vapor stream, but is not necessary here.
4. Less vapor friction through condenser, important when low vacuum is used.
5. Deeper trap for condensate return, eliminating danger of boiling back.

There are these additional advantages if the electric internal heater is used:

1. More uniform boiling with extremely small vapor bubbles.
2. Constant and thorough agitation of liquid.
3. Impossibility of stagnant liquid collecting near sample cock of flask.
4. Better control ensuring uniform rate of distillation. Constant-pressure control readily applied.
5. Smooth vacuum runs without bumping.

RESULTS

Figures 3 to 5 show the results of three of the many curves plotted with this apparatus. They are all near normal atmospheric pressure, 750 mm. and the results given in Table I are taken at even liquid composition from curves drawn with a large number of experimental points. The results are in weight per cents of the more volatile liquid rather than the mole per cents more often used in engineering calculations.

All of the materials used in obtaining these data, including the formic acid, were purified from good original sources to a high degree by distillation methods in apparatus previously described (3). Very close boiling cuts were obtained for the experimental work. The three curves in Figures 3 to 5 illustrate the three usual types of binary vapor composition curves: the benzene-acetic acid mixture having a minimum constant-boiling mixture, the formic acid-water mixture having a maximum constant-boiling mixture, and the acetic acid-acetic anhydride mixture being normal in that it has no constant-boiling mixture.

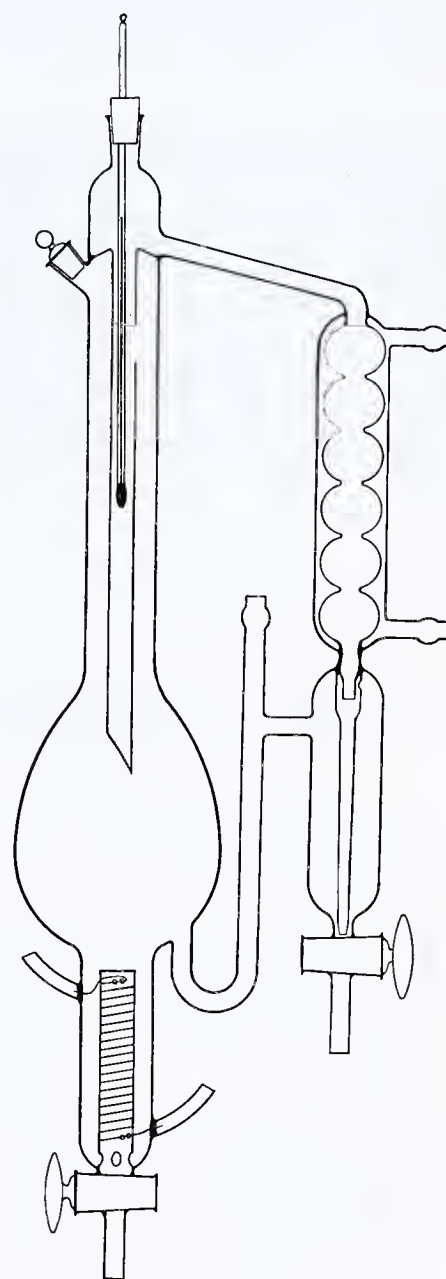


FIGURE 2. DIAGRAM OF APPARATUS

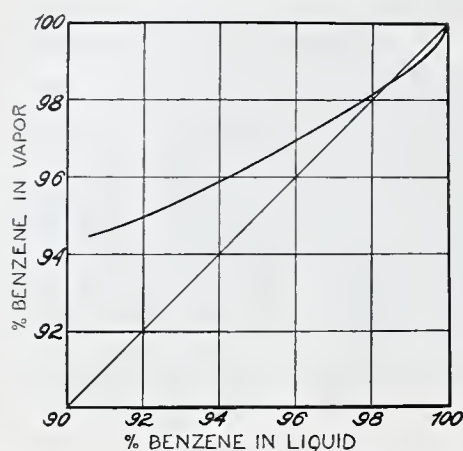


FIGURE 3. BENZENE AND ACETIC ACID

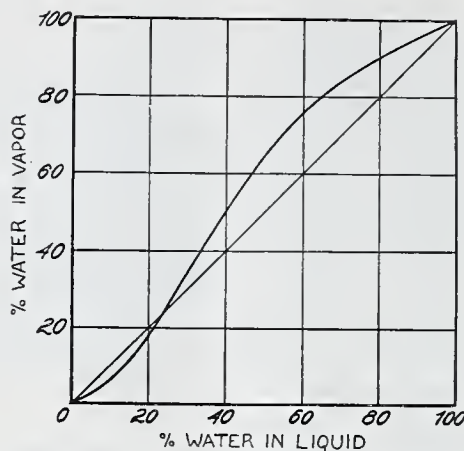


FIGURE 4. WATER AND FORMIC ACID

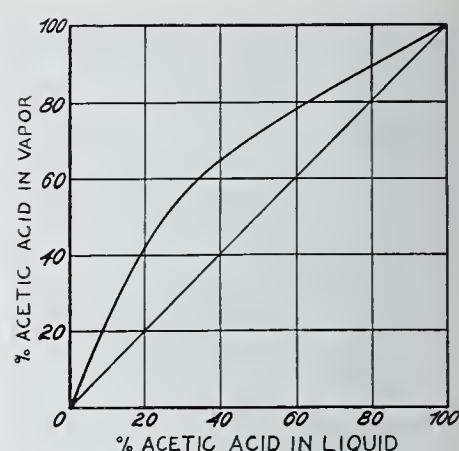


FIGURE 5. ACETIC ACID AND ACETIC ANHYDRIDE

In the previous paper (2) the constant-boiling mixture of benzene and acetic acid was not noted, since it is higher in benzene than any of the points plotted. The portion of the curve near the azeotropic point, which is at 98.5 per cent benzene, has been carefully plotted on an enlarged scale. Formic acid forms with water one of the comparatively few binary mixtures having a constant-boiling or azeotropic mixture of maximum boiling point. Bergstrom (1) has plotted the vapor composition curve for mixtures of the liquid higher in water content than the azeotropic mixture, and his curve falls just below that drawn in the upper loop.

The acetic acid-acetic anhydride curve is typical of a normal binary mixture having no constant-boiling or azeotropic mixtures.

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Potash Analyses

Study of Methods for Eliminating Errors in Determination of Potash in Fertilizer Mixtures High in Phosphoric Acid

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IN RECENT years it has been recognized by many analysts that fertilizer mixtures high in phosphoric acid present difficulties in the determination of the potash content. Since 1925 reports have been published by Kerr (5), Bible (1), Fraps (3), Haigh (4), and Lockhart (6).

Workers on the problem attribute potash losses to the formation and attack of metaphosphates on silica, either the silica dishes used during evaporation and ignition, or soluble silica that may sometimes be present in amounts sufficient to cause trouble, even though evaporation and ignition may be carried out in platinum. The first four chemists mentioned have tried to solve the trouble by some method of removing the phosphoric acid before the ignition step, whereas Lockhart minimizes the metaphosphate attack by carefully controlling the ignition temperature.

Removal of the phosphoric acid by any of the suggested methods prevents most of the attack on the silica dishes. In 1926 the writer determined quantitatively the losses in the weight of silica dishes resulting by use of the official Lindo-Gladding method and a modified method (1) in which the phosphoric acid was removed with magnesium oxide. Six new dishes were obtained for the tests from a leading manufacturer of silica ware. Three dishes were used by the official Lindo-Gladding method and three by the modified method on regular factory mixtures until each dish had been used seven times. The three dishes used in the official method lost in

weight 0.0339, 0.0427, and 0.0444 gram. The three used in the modified method lost in weight only 2.7 per cent as much.

Much of the silica dissolved or loosened from the silica dish appears as an impurity in the potassium chloroplatinate, even if the dissolved residue is filtered prior to the addition of chloroplatinic acid. By dissolving the potassium chloroplatinate from the crucible with hot water, one can frequently find much insoluble impurity. In some cases the silica is sufficient to make filtration very difficult.

The modified methods providing for removal of the phosphoric acid, on the other hand, give precipitates of potassium chloroplatinate completely soluble in water. The ignited residue likewise dissolves in water much more readily.

Removal of the phosphoric acid prior to ignition prevents losses of potash due to formation of insoluble potassium phosphosilicates or of potassium metaphosphate, which is soluble with difficulty. Results obtained by the modified methods usually do not fall far short of the theoretical potash content.

The only objection to the use of any of the methods providing for the removal of the phosphate is that there appears to be a greater loss of potash due to occlusion, because of the additional precipitate that results, and there appears to be no practical way of recovering the occluded potash. Although the modifications contribute to refinement of the method, still the full potash values cannot be obtained.

The writer has attempted to prevent metaphosphate formation and attack in another way, without removing the phosphates, by having present at the time of ignition sufficient combined sodium and potassium to give the orthophosphate. In practice, it requires only the addition of a little potash-free sodium hydroxide to the aliquot during evaporation.

As early as 1903, Carpenter (2), acting as referee on fertilizers, suggested "the use of a little hydrochloric acid to liberate occluded potash and neutralization with sodium hydroxide instead of ammonium hydroxide to prevent occlusion of potash, which is usually found when using ammonia and ammonium oxalate." He reported that the results were promising. However, no method involving the use of sodium hydroxide was adopted. It is unfortunate that the work was not continued, for neutralization with sodium hydroxide instead of with ammonia results in more nonvolatile bases to combine with the phosphate, and tends to keep the phosphate from going to the meta form.

In trying out the effectiveness of sodium hydroxide in preventing metaphosphate attack, the phosphatic compounds diammonium phosphate, treble superphosphate, and nitrophoska were used. The potash determinations were carried out only to the point where the ignited residue could be examined for form and amount of phosphorus, and the insolubility of the ignited residue in water acidified with a little hydrochloric acid. The official Lindo-Gladding method in silica dishes gave residues which left much white water-insoluble material after long digestion with water acidified with hydrochloric acid. About one-third of the phosphorus was volatilized, both from platinum and silica dishes.

When 2 cc. of normal sodium hydroxide were added to a solution of diammonium phosphate containing 0.1140 gram of phosphorus pentoxide, evaporated and ignited in silica, the solution was almost clear, and no phosphorus was volatilized. When the sodium hydroxide was increased to 4 cc., the solution was perfectly clear, and no phosphorus was volatilized. These tests show the benefit of sodium hydroxide additions in the presence of enough phosphorus to form much metaphosphate.

A comparison of methods on a mixture of potassium chloride and superphosphate, with 0.0730 gram of phosphorus pentoxide in the aliquot used for analysis, gave:

METHOD	K ₂ O COR. FOR IMPURITY %	IMPURITY %
Official Lindo-Gladding	5.82	0.46
	5.84	0.28
	5.88	0.36
Phosphorus removed with MgCl ₂	5.81	0.02
	5.86	0.03
Phosphorus removed with MgO	5.80	0.03
	5.80	0.02
Normal NaOH, 3 cc., used	5.89	0.11
Normal NaOH, 6 cc., used	5.95	0.11
	5.89	0.07
	5.88	0.05

A mixture of potassium chloride and superphosphate, ammoniated with aqua ammonia, with 0.0592 gram of phosphoric pentoxide in the aliquot used for analysis, gave:

METHOD	K ₂ O COR. FOR IMPURITY %	IMPURITY %
Official	5.40	0.17
Phosphorus removed with MgO	5.27	None
Normal NaOH, 6 cc., used	5.40	None

Several other mixtures of ammoniated superphosphate with from 0.0370 to 0.0420 gram of phosphorus pentoxide in the aliquots taken were tested by the official method and also by adding 1 cc. of normal sodium hydroxide during evaporation. The residues by the official method would not burn white, would not dissolve completely, and silica retarded filtration. The use of sodium hydroxide gave white residues easily soluble in water, and the potassium chloroplatinate was free from silica.

Analyses were also carried out on preparations with known potash content. A solution of pure potassium chloride was made, containing 0.25 gram to 50 ml. of solution. That amount was put into each of three 250-ml. volumetric flasks. Into two of the flasks was leached the water-soluble portion of 2.25 grams treble superphosphate. To the third flask no phosphate was added. With the volume in each flask approximately 200 ml., ammonia and ammonium oxalate were added. To one of the flasks containing phosphate, about 1 gram of magnesium oxide powder was added. All three were then finished as in the Lindo-Gladding method.

Two aliquots were taken from the flask containing phosphate but no magnesium oxide. One was used following strictly the official Lindo-Gladding method. To the other aliquot was added 0.09 gram of sodium hydroxide in solution, and the experiment was then finished in the same way. The only difference in the methods employed was the use of sodium hydroxide in the one.

The potash contained in equivalent amounts of the treble superphosphate and in the reagents was determined and deducted from the final results.

The potash recovery by the method using magnesium oxide was 99.03 per cent. The official Lindo-Gladding method gave 97.9 per cent recovery, whereas the combination of the Lindo-Gladding method with a little sodium hydroxide gave the best recovery, 99.36 per cent.

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PROPER FRACTIONATION WILL REDUCE COST OF MANUFACTURING GASOLINE. The cost of manufacturing gasoline from high-sulfur crude oils may be reduced by proper fractionation methods, is indicated as the result of a study made by the United States Bureau of Mines, Department of Commerce. The importance of proper fractionation in the manufacture of gasoline from crude petroleum is evidenced when gasoline is being made from crude oils containing relatively large proportions of sulfur. Such gasolines usually require considerable chemical treatment after distillation from the crude oil to meet trade requirements as motor fuels.

The cost of the treatment necessary to prepare an acceptable motor fuel is generally the major difference between the cost of manufacturing gasolines from different crudes. The actual cost of distilling equal amounts of gasoline from different crudes

varies little, for the amount of heat required to vaporize a gallon of gasoline of the same gravity from different crudes is nearly constant. It must be recognized, however, that depreciation of the distillation equipment is greater with some crudes than others.

An investigation has therefore been conducted by the Petroleum Experiment Station at Bartlesville, Okla., which is maintained by the Bureau of Mines and the State of Oklahoma, to determine the effect good fractionation would have on the manufacture of gasoline from crude oil containing sulfur, for, if high-sulfur crudes can be distilled so that the cost of preparing gasoline suitable for motor fuel will be reduced by eliminating some of the chemical treating costs, the commercial value of these crudes will be increased proportionally. Preliminary results of the investigation are regarded as quite encouraging.

Determination of Copper

Observations on Clarke and Jones Method

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THE importance of minute traces of copper in biological processes and products has been the subject of numerous researches during the past few years. Of the many analytical methods available for the detection and estimation of small amounts of copper, the procedure of Biazzo (2) in one of its many modifications (1, 4, 5, 8) is usually followed. The method is accurate under most conditions and capable, in the hands of an experienced analyst, of yielding concordant results.

It is, however, time-consuming and involves an extraction of a copper thiocyanate-pyridine complex with subsequent quantitative recovery of all or a known portion of the immiscible solvent.

The analytical method proposed by Clarke and Jones (3) appeared to offer distinct possibilities as a micromethod for copper. The procedure consisted essentially of adding to a very dilute sulfuric acid solution of copper, ammonium persulfate, dimethylglyoxime, silver nitrate, and pyridine. In the presence of copper these reagents produce a "permanganate pink" whose intensity varies with the copper concentration. The authors advise that comparison with standards be made without undue delay because of the tendency of the color to fade.

The Clarke and Jones method for copper is suitable only under carefully controlled conditions. Because of the many factors contributing to color variation for fixed amounts of copper, it is not suitable for general use. It is recommended that, if the method is used, a series of secondary potassium permanganate standards be established. Inasmuch as numerous factors appear to contribute to the variation in color and color intensity, it is advisable to check the permanganate standards against known amounts of copper under the conditions of the analysis.

directly in the solution. Such a combination would obviate the necessity of ashing and would make the determination suitable for field use. Accordingly, a study of the variables was made in an effort to define the limits of the method.

The concentration of the color produced during the course of the trial reactions and determinations was measured by means of an Eastman Universal Colorimeter (6, 7). "This instrument operates on the subtractive principle and any de-

sired color may be obtained in the comparison field by the subtraction of certain parts of the white light used for the illumination of the comparison field. This subtraction is accomplished by the use of dyed gelatin wedges. By using three wedges, each of which absorbs one of the three additive primaries, any desired amount of each primary may be subtracted from the white light." It was found that the pink color produced by the Clarke-Jones reaction matched almost exactly that transmitted through the — green wedge of the instrument. Consequently, it was possible to translate the intensity of red in the solutions under examination directly into the reading of but one scale. Inasmuch as the scale readings were reproducible, the instrument served as a fixed standard to which all observations and determinations could be referred.

Standard copper solutions were prepared by dissolving weighed amounts of recrystallized copper sulfate in conductivity water and diluting to known volumes. Stock solutions so prepared were checked iodometrically against thiosulfate solutions standardized on pure electrolytic copper. Ammonium persulfate and silver nitrate were of reagent quality and were used without further purification. The pyridine was redistilled. Because ordinary distilled water which had been stored in tin-lined copper tanks gave rise to the characteristic pink color when used in conjunction with the test reagents, care was taken to make all dilutions with freshly prepared "conductivity" water. The dimethylglyoxime was obtained from the Eastman Kodak Company and was used without further purification. A saturated solution of dimethylglyoxime in 95 per cent ethyl alcohol was used throughout the work. The alcohol was redistilled and free from interfering traces of acid. Blank determinations established the purity of the reagents.

It was ascertained early that if the concentration of pyridine was varied but slightly for fixed concentrations of the remaining constituents, the intensity of the color varied widely. Figure 1 illustrates the variation in color concentration produced by varying the pyridine concentration. The points were obtained by plotting colorimeter-scale readings against cubic centimeters of 10 per cent pyridine added. To 50 cc. of solution, prepared by diluting suitable volumes of the copper standards with conductivity water, were added 1 cc. of 0.4 *N* sulfuric acid, 0.5 gram of ammonium persulfate, 0.5 cc. of dimethylglyoxime solution, and 0.25 to 0.3 cc. of 0.5 per cent silver nitrate. Following thorough mixing, the pyridine was

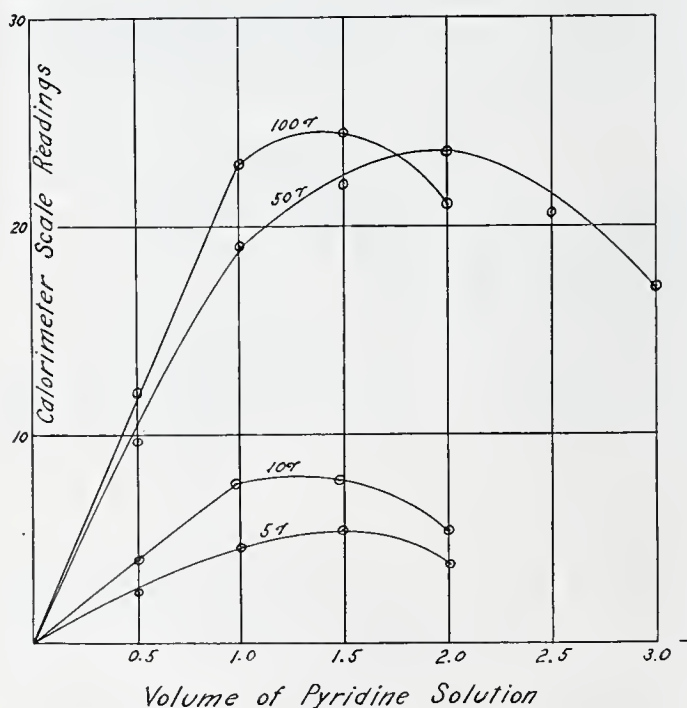


FIGURE 1. VARIATION IN COLOR CONCENTRATION PRODUCED BY VARYING PYRIDINE CONCENTRATION

Inasmuch as the determination is carried out in a slightly acid solution, it appeared to the writers that a wet combustion could be made upon the organic samples, and after proper adjustment of the acidity the copper could be determined

added and the Nessler tube inserted in the colorimeter. Five minutes were allowed to elapse between the addition of the pyridine and the final reading. It will be noted that the color intensity reached a maximum when 1.5 cc. of pyridine solution were used, and fell off rapidly with higher concentrations of the base. It was found that if the initial sulfuric acid concentration greatly exceeded 0.008 *N* the coloration of the solution was very faint and fugitive. The addition of a corresponding amount of pyridine did not stabilize the color.

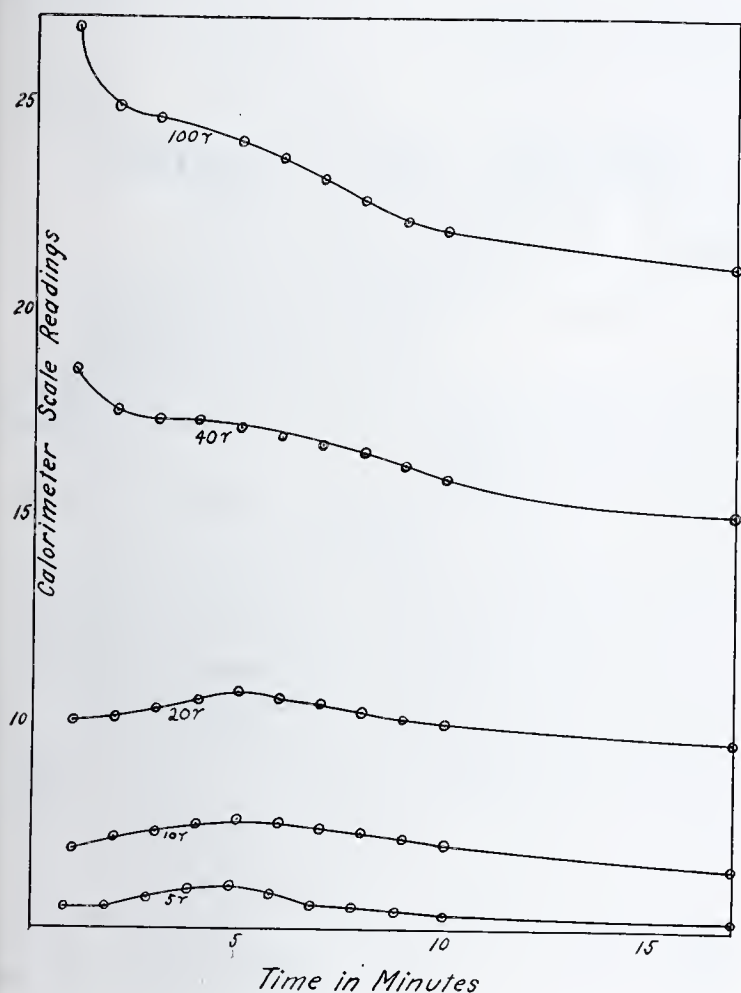


FIGURE 2. COMPARISON OF UNKNOWN WITH STANDARDS

The four curves are illustrative of a large number of data obtained for concentrations of copper between 5 and 100 γ per 50 cc. of solution ($1\gamma = 0.001$ mg.). Pyridine in amounts greater than 3 cc. of 10 per cent solution caused rapid fading. One series of observations indicated that if 5 cc. of the base were used, the scale readings dropped approximately 25 per cent in less than 10 minutes. A significant decrease in the initial concentration of sulfuric acid gave erratic results. An effort was made to find a buffer mixture which would maintain the acidity of the solution at such a value as to provide maximum color development. All such buffers studied either detracted from the sensitivity of the reaction or caused too rapid fading.

Clarke and Jones made reference to the phenomenon of color fading and recommended a rapid comparison of unknowns with standards in order to minimize the error from this source. Inasmuch as the instrument used in the present work was particularly well adapted to a quantitative evaluation of color change, a series of periodic observations was made on a group of samples. The results of some of the observations are shown in Figure 2. The solutions under observation were prepared in the regular manner and the wedge readings recorded for intervals of 1 minute. One cubic centimeter of pyridine was used in each case. It will be noted that the fading in dilute solutions was slight. It was

observed that when the copper concentration was less than 30 γ per 50 cc., the color reached a maximum 5 minutes after the addition of the pyridine and then faded slowly. In higher concentrations, however, the color intensity reached a maximum almost immediately after the addition of the base and faded rapidly.

Because of the difficulty of making an accurate color comparison between two solutions, each of which is fading at a different rate, it was deemed advisable to establish a series of secondary standards whose color would closely approximate that produced by known amounts of copper. Fortunately the color of dilute permanganate solutions is almost identical with that produced by the Clarke-Jones reaction. The instrument was calibrated in terms of copper by treating known amounts of copper in the manner described. One cubic centimeter of 10 per cent pyridine solution was used and 5 minutes were allowed to elapse between the mixing of the pyridine and the recording of the color concentration. The instrument was then calibrated in terms of 0.002 *N* potassium permanganate by adding varying amounts of the permanganate solution to 50 cc. of conductivity water. The relationship between copper and the volume of permanganate required to match the color exactly is shown in Figure 3. This curve has been checked independently by F. Norman Pansch working in this laboratory. It should be mentioned that this relationship holds only under the conditions specified. If

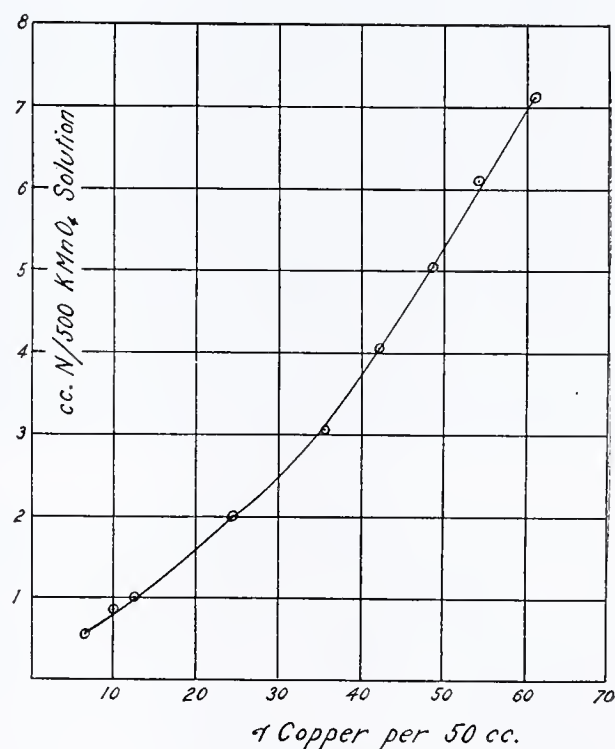


FIGURE 3. COPPER *vs.* VOLUME OF PERMANGANATE

the initial concentration of sulfuric acid exceeds 0.008 *N*, the colors will be lighter. It is recommended that the permanganate standards be checked under the conditions to which the determination is being adapted. The permanganate standards may be stabilized by adding to each tube a small amount of potassium iodate and sulfuric acid.

Silver nitrate greatly in excess of the quantity recommended by Clarke and Jones tends to promote rapid fading and introduces a yellow coloration which interferes with accurate estimation of the copper present. Significant increases in the initial concentrations of ammonium persulfate causes rapid fading in a short time, owing, no doubt, to the increased acidity resulting from the decomposition of this oxidizing agent. Sulfates and nitrates appear to be without effect on the determination. Sodium sulfate, magnesium sulfate,

calcium sulfate, and potassium nitrate in concentrations as high as 2 mg. per cc. do not appreciably affect the intensity or the stability of the color. Although the turbidity produced by silver chloride may be discharged with an excess of pyridine as recommended by the original authors, the color intensity for a given amount of copper is greatly reduced. If the chloride content exceeds 0.5γ per cc., the method is not reliable and should be used with caution. Iron in amounts greater than 2γ per cc. introduces serious error. Cobalt in concentrations greater than 0.02γ per cc. likewise renders the determination unreliable.

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The Metal Tube in Micro- and Semi-microcombustion Analysis

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PREVIOUS work (1, 2) showing the advantages of metal tubes for macrocombustion analysis has been confirmed by Klatschin (4). The present communication deals with the use of metal tubes for micro- and semi-microcombustion analysis.

Three types of copper combustion tubes provided with water-jacketed ends were used. Each was especially adapted to the analysis of compounds of a certain type. A silver tube, applicable to either micro- or semi-microanalysis, was used for compounds containing halogen. Qualitative tests showed that such a tube, with a filling composed of copper oxide and silver-coated copper oxide, completely retained the halogen. A boat inserter was designed to facilitate the introduction of the boat into the combustion tube. A similar inserter employed as a boat in the nitrogen determinations aided in the introduction of the sample mixed with copper oxide.

The writers of the present article have found that the use of metal tubes embodies in micro- and semi-microcombustion analysis the same advantages (1, 2) over tubes made from other materials, as previously found in macroanalysis.

COMBUSTION TRAIN

The current of air, oxygen, or nitrogen to be regulated and freed from impurities was passed through a pressure regulator (5), a metal preheater (2), a bubble counter (see Figure 1), and an absorption train made from the same reagents as are used in the weighed absorption train. Since a considerable amount of time was required to sweep out the complete apparatus when changing from oxygen to air, nitrogen to oxygen, etc., a double gas line was set up and the gases were brought together directly in front of the combustion tube. The gases were controlled by pressure regulators and screw clamps on the gas lines in front of the bubble counters. When one line was in use, the other was shut off with the screw clamp. Diffusion at the three-way connection of the gas lines was made negligible through the use of capillary tubing.

The furnace used in this investigation was the ordinary three-element electric furnace commonly employed in macro work, except in the case of copper tube I. In this instance, a furnace with one 18-cm. element and two 10-cm. elements was employed. With an electric furnace and the double gas line, the minimum time necessary for accurate microanalysis of benzoic acid was found to be 15 minutes.

Pregl's absorption tubes were used in microdeterminations, and similar tubes of greater capacity were used in semi-microanalyses. By using as counterpoises a duplicate set of absorption tubes filled in the same manner as those of the

absorption train, fluctuations in weight caused by changing external conditions during the time necessary for weighing were found to be negligible.

CARBON AND HYDROGEN DETERMINATIONS IN VARIOUS COMPOUNDS

COMPOUNDS WITH OXYGEN AS ONLY ADDITIONAL ELEMENT. For strictly microdeterminations (as distinguished from semi-micro) in such compounds, the assembly shown in Figure 1 was found most satisfactory. The copper combustion tube (I) had an inner diameter of 5 mm. and a length of 70 cm. It was provided with water-jacketed ends and protected externally by a jacket of nickel. One end of the tube was slightly distended and reamed out in order that a rubber stopper might be inserted. The absorption end of the tube was threaded. Into this was screwed, with a solder seal, a threaded bronze "adapter" with an outer diameter of 3 mm. and a neck 2.5 cm. long. This eliminated the necessity of a rubber stopper at the absorption end of the tube. It was thus unnecessary to open the absorption end of the tube, the

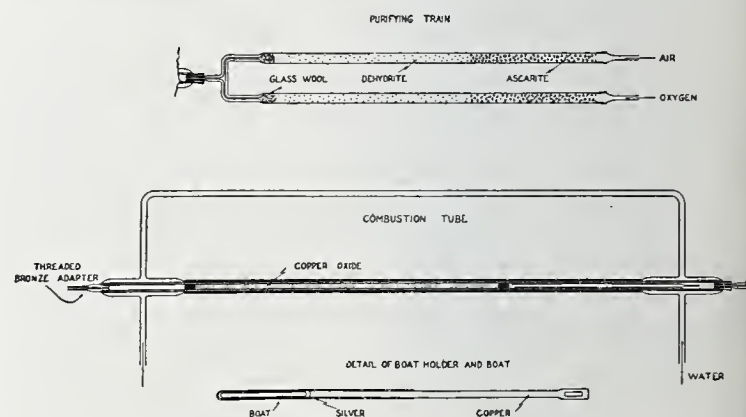


FIGURE 1. DIAGRAM OF ASSEMBLIES

absorption train was more easily attached, and the temperature maintained by the adapter through its conductivity prevented the condensation of water at the entrance of the dehydrite tube. The combustion tube was filled with copper oxide in the usual manner.

In order to facilitate the introduction of the boat into the combustion tube and to avoid spilling the sample or overturning the boat, a boat carrier was designed. This consisted of a copper rod 4 mm. in diameter, to one end of which was attached with silver solder a piece of silver shaped to hold the boat. The copper rod was then silvered for a distance of 5 cm.

from the silver receptacle to prevent the deterioration of the copper rod through oxidation. Boats were made of silver.

The results of five consecutive analyses of sucrose carried out in this copper tube are tabulated in Table I (A).

TABLE I. CARBON AND HYDROGEN DETERMINATIONS

DETN.	TUBE	SUBSTANCE	APPROX. WT. Mg.	FOUND		CALCD.	
				C %	H %	C %	H %
(A)	Copper I	Sucrose	5	42.16 ^a	6.47 ^b	42.08	6.48
(B)	Copper II	Nitrobenzyl cy- anide	20	59.20	3.76	59.24	3.73
		Nitrotoluene	20	61.24	5.19	61.28	5.15
		Dinitrotoluene	20	46.10	3.28	46.14	3.32
(C)	Silver	<i>o</i> -Chlorobenzoic acid	10	53.60 ^c	3.26 ^d	53.68	3.20
(D)	Silver	<i>o</i> -Chlorobenzoic acid	70	53.69 ^e	3.24 ^f	53.68	3.20
(E)	Copper III	Sucrose	10	42.01	6.52	42.08	6.48
		Benzoic acid	10	68.85	5.00	68.83	4.96
		Dinitrotoluene	10	46.03	3.45	46.14	3.32
		Sulfonal	10	36.74	7.14	36.80	7.07
		<i>p</i> -Bromobenzoic acid	10	41.76	2.61	41.80	2.51
		Thiocarbanilide	10	68.16	5.43	68.37	5.30

^a Average of 42.24, 42.16, 41.89, 42.25, 42.28.

^b Average of 6.44, 6.51, 6.41, 6.41, 6.57.

^c Average of 53.54, 53.50, 53.70, 53.56, 53.68.

^d Average of 3.21, 3.31, 3.31, 3.17, 3.28.

^e Average of 53.55, 53.88, 53.80, 53.52.

^f Average of 3.23, 3.22, 3.26, 3.24.

COMPOUNDS CONTAINING NITROGEN. The copper tube (II) used in these determinations differed from the one described above only in the size of the tube and the replacement of the bronze adapter with a rubber stopper to facilitate the introduction of the reduced spiral. The tube had an inner diameter of 7 mm. and a length of 100 cm. For analyzing compounds containing nitrogen, the oxidized spiral was replaced by a similar spiral which had previously been reduced to metallic copper in a current of carbon monoxide. The combustion was first carried out in a current of nitrogen, then in a current of oxygen, and finished with air, in the usual way. A tube of this size is also adaptable to semi-micro-analysis. Results of analyses of compounds containing nitrogen are tabulated in Table I (B).

COMPOUNDS CONTAINING HALOGEN. Copper tube II, described for compounds containing nitrogen, was found satisfactory for the analysis of compounds containing bromine. The fillings were identical except that the oxidized copper spirals were replaced by silver ones. However, since compounds containing chlorine tend to corrode the copper tube, investigations were started along a different line.

Pregl (6) and others have accepted silver as the best reagent for the retention of halogen. Thus, a combustion tube composed of this metal should prove ideal for such analysis, as has been found to be the case. The silver combustion tube had an inner diameter of 7 mm., a length of 100 cm., and a side-wall thickness of 1.5 mm. At the current prices of fine silver, the cost of the metal in such a tube is about \$6.00. A tube of this size has the advantage of being suitable for semi-micro work also. The ends were water-jacketed and the tube was made more rigid by an external iron jacket. This tube can be heated safely to temperatures well above those necessary for the ordinary analysis.

The filling for the tube consisted of a mixture of one-third copper oxide and two-thirds copper oxide coated with silver. The latter was prepared as follows: Seventy grams of copper oxide were mixed with 30 grams of pulverized silver nitrate. Small portions of this mixture were introduced into a fire-clay crucible, and with constant stirring were heated over an oxy-gas flame until all evidence of the evolution of the oxides of nitrogen had ceased. This resulted in a rough, bright coating of silver on the copper oxide. Such a filling should suffice for a large number of analyses. Silver boats were used to hold the sample. This tube and filling work equally well for compounds not containing halogen. With proper care, the tube should last indefinitely. The results of a series of

consecutive micro-analyses of *o*-chlorobenzoic acid carried out in this tube are given in Table I (C).

A series of semi-microanalyses of *o*-chlorobenzoic acid was also carried out with this tube and filling. The weighing was done on a sensitive analytical balance and was accurate to approximately 0.02 mg. The results of these analyses are to be found in Table I (D).

DETERMINATIONS USING PREGL'S "UNIVERSAL" FILLING. The copper tube used in this instance (III) was essentially the same as the one used with nitrogen except that it had a bore of 5 mm. and an additional jacket. This jacket, replacing Pregl's heating mortar (7), was brazed to the copper combustion tube, adjacent to one of the water-jacketed ends. It had a diameter of 50 mm. and was 10 cm. long. A copper tube 20 mm. in diameter and 30 cm. long was brazed to this jacket perpendicular to the combustion tube. It served as a condenser for the constant-boiling liquid used in the jacket. Cymene, advocated by Pregl, was found to be satisfactory.

The results obtained with this tube, using Pregl's "Universal" filling, were not as uniformly accurate as with the other tubes described, unless extreme care was exercised. It is recommended for the carbon and hydrogen determinations of compounds containing sulfur. The results of analyses of different types of compounds are given in Table I (E).

DETERMINATION OF NITROGEN

Copper combustion tube II was used for the determination of nitrogen by the Dumas method and was loaded in the ordinary way with copper oxide and reduced spiral, with the following modifications: The relatively long reduced copper spiral was re-oxidized for half its length and inserted in the tube with the oxidized end toward the azotometer. This section of the spiral served to reoxidize any trace of carbon monoxide which might be formed by passing carbon dioxide over the reduced portion of the spiral. An unusual feature was the use of a combination boat, carrier, and filler for the front part of the tube. This was made of monel metal and was 18 cm. in length. It was of the general shape of the boat-holder previously described and proved to be a very satisfactory means of introducing into the tube, mixed with powdered copper oxide, the substance to be analyzed. The assembly for generating carbon dioxide was essentially the same as that described by Fisher (3). The azotometer was the same as that used by Pregl (8). Results with this assembly are given in Table II.

TABLE II. NITROGEN DETERMINATIONS

TUBE	SUBSTANCE	APPROX. WT. Mg.	N FOUND	N CALCD.
			%	%
Copper II	Acetanilide	11	10.34	10.37
	Dinitrotoluene	8	15.35	15.39
	Compound C ₂₄ H ₂₁ ON	30	4.09	4.13

ACKNOWLEDGMENT

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Chromous Sulfate as Reducing Agent in Volumetric Determination of Iron

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CHROMOUS salts, which are undoubtedly very powerful reducing agents, have come into prominence for use in deoxidation methods of analysis within the last few years. Although this property of bivalent chromium was known at a comparatively early date, chromous chloride having been employed in gas analysis (12), it was not until recently that Buehrer and Schupp (2) demonstrated the feasibility of utilizing it in certain volumetric processes. Since then, methods depending upon reduction by a chromous compound have been brought out for the estimation of various elements either alone or in admixture with one or more others (13).

This present contribution consists in preparing a solution of chromous sulfate of the requisite purity and stability by a well-known convenient procedure, devising a reliable apparatus for storing and using the solution so obtained, and studying the reduction of a ferric salt at such temperatures as usually prevail in a working room.

CHROMOUS SULFATE SOLUTION USED

PREPARATION. A number of investigators (2, 10, 12, 13) have prepared chromous salts, utilizing in all a variety of processes but, as a rule, the resulting product did not show a satisfactory degree of stability.

Since others (11) have demonstrated that chromium can be completely reduced to the bivalent condition by means of the Jones reductor, certainly, when operating on the analytical scale, a slightly modified form of this familiar apparatus was adopted for obtaining a solution of chromous sulfate. In short, 5 liters of a solution of potassium dichromate, containing 75 grams of the salt, which had been purified by two recrystallizations of the c. p. material, and 125 cc. of sulfuric acid (sp. gr., 1.84) were passed through a column of amalgamated zinc (40 cm. long and 1.9 cm. wide) at the rate of about 40 cc. per minute, the deoxidized liquid being caught in a 6-liter flask through which a stream of carbon dioxide was maintained during the entire operation. This solution was thoroughly mixed by continuing the flow of the carbon dioxide, and when cool, it was charged into the stock bottle of the storage apparatus previously employed by Thornton and Wood (9) for titanous sulfate.

It can be calculated from the reaction that the chromous sulfate solution was not over 0.18 *N* with respect to sulfuric acid. According to certain authorities (1) the acidity of the solution plays an important role in the decomposition of chromous salts, hydrogen being liberated in sufficiently acid media; hence it is reasonable to suppose that the gratifying degree of stability exhibited by the solution was due in some measure, at least, to its low concentration of free sulfuric acid.

Although when actually tested, the solution was found to be

Chromous sulfate solutions which are suitable for analytical work may be conveniently prepared from potassium dichromate (and doubtless from other chromium compounds) by means of the Jones reductor.

*Chromous sulfate in sulfuric acid not stronger than 0.18 *N*, if stored properly, can be kept for a period of 2 months without undergoing an appreciable change in titer; and it is not necessary to remove the dissolved zinc.*

Iron in cold solution can be readily determined by potentiometric titration with chromous sulfate, provided a small quantity of potassium thiocyanate be added. It is believed that the results so obtained are very near to the true values.

0.067 *N* instead of 0.1 *N*, as originally intended, this does not necessarily indicate that the reduction was incomplete, for the chromous salt probably suffered some oxidation from exposure to air during the transfer to the storage bottle.

TITRATION APPARATUS. As solutions of chromium compounds (especially the chromic salts) are highly colored, it became practically necessary to determine the end point electrometrically in the present work. A 250-cc. wide-mouthed Erlenmeyer flask served as the reaction vessel. The Roberts titration outfit (3), whose potentiometer

is manufactured by the Leeds and Northrup Company, was used for following the relative electromotive force of the solution as the experiment proceeded. The electrodes, however, were somewhat modified, particularly in that the calomel half-cell was made larger and the vertical part of the glass tube covering the platinum electrode, down which the carbon dioxide passed, was lengthened so that it dipped well into the solution. The carbon dioxide thus served the twofold purpose of stirring the liquid and protecting it against atmospheric oxidation. Finally, the flask was closed with a four-holed rubber stopper through which the buret tip, the two electrodes, and the outlet tube passed.

PERMANENCE OF STANDARD SOLUTION. An approximately 0.1 *N* solution of ferric ammonium sulfate was prepared by dissolving 48.2 grams of the crystalline salt $[\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$ in water, adding 50 cc. of concentrated sulfuric acid, and diluting to 1000 cc., the function of the acid being to prevent the formation of basic sulfate of iron. Any ferrous salt that might have been present was oxidized with the least possible amount of 0.1 *N* potassium permanganate. The solution was then boiled to decompose the small excess of permanganate, cooled, and allowed to stand for 2 days, when it was stored in a glass-stoppered bottle and kept in the dark.

To 20 cc. of the ferric alum solution 12 cc. of sulfuric acid (1 to 1) and 50 cc. of water were added. The resulting solution was heated to the boiling point, the flask was set in place under the buret, and the system was swept with carbon dioxide for 10 minutes. Throughout the entire series of operations a small flame was kept under the flask to maintain the test solution at a temperature of 80° to 100° C. When all but about 2 cc. of the required amount of chromous sulfate had been introduced, no further addition was made until a constant reading on the potentiometer had been obtained, after which the standard reagent was added slowly till the end point was actually reached.

In this way it was found that the solution did not undergo an appreciable change of titer during a period of 2 months.

PURITY OF SOLUTION. Although the use of an iron-free chromous salt is not necessary in the present case, contamination by this element would doubtless interfere in certain other

analytical processes (4). Accordingly, it was thought desirable to have at hand a convenient and reliable method for detecting and, if possible, determining the amount of this well-nigh ubiquitous substance.

Kolthoff and Tomiček (5) have estimated small quantities of iron in titanous chloride solutions by titrating potassium dichromate electrometrically with the titanous salt, and by this method they were able to determine as little as 0.25 per cent of iron (reckoned on the content of trivalent titanium).

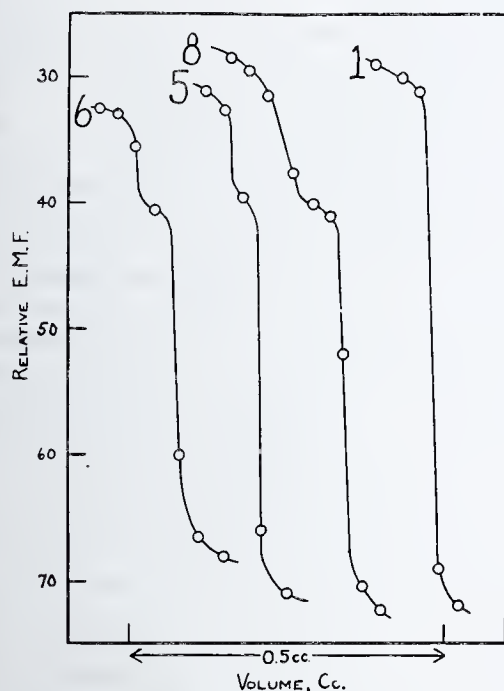


FIGURE 1. TITRATION CURVES OF CHROMOUS SULFATE AGAINST POTASSIUM DICHROMATE

If iron is present in sufficient amount, two breaks in the titration curve can be observed: the first appears immediately after the complete reduction of the dichromate, and the second just after the deoxidation of the ferric salt (formed from the ferrous salt originally present in the titanous chloride solution at the expense of the dichromate). Consequently, the volume of standard reagent used between the first jump and the second corresponds to the iron content of the solution.

An exactly analogous procedure was followed in order to test the solution of chromous sulfate for iron. A 0.1 *N* solution of potassium dichromate was prepared by dissolving the requisite amount of the salt (purified as described above) in water and diluting to the proper volume. A measured quantity of this solution was acidified with 12 cc. of sulfuric acid (1 to 1) and 90 cc. of water were added to it. An accurately known amount of iron was then intentionally introduced, and the composite solution was titrated in the same way as the ferric alum except that the reduction was carried out more slowly.

TABLE I. TITRATION OF CHROMOUS SULFATE AGAINST POTASSIUM DICHROMATE

No.	K ₂ Cr ₂ O ₇ TAKEN Cc.	CrSO ₄ REQUIRED ^a Cc.	Fe TAKEN Gram	Fe FOUND Gram
1	35	53	None	None
2	35	53	None	None
3	5	7.5	0.00007	None
4	5	7.5	0.00012	None
5	5	7.5	0.00013	0.00015
6	5	7.5	0.00020	0.00022
7	5	7.5	0.00020	0.00022
8	5	7.5	0.00041	0.00037
9	5	7.5	0.00042	0.00030

^a Total volume; approximate only.

The results are given in Table I, and some of the titration curves are plotted in Figure 1, the numbers of the curves corresponding to the numbers of the experiments. In experi-

ments 1 and 2, however, enough dichromate (35 cc.) was taken to react with 53 cc. of chromous sulfate, but no iron was added. On actually titrating, none was found. From these findings it is logical to conclude that the chromous sulfate solution, which had been prepared with the aid of c. p. zinc, was virtually free from iron, or that it contained, at a maximum estimate, less than 0.00015 gram per 50 cc. of solution.

TITRATION OF IRON

Titration were next conducted, first, with the solution of ferric salt hot, and then with it cold, the procedure being otherwise the same as that described above.

On comparing the results obtained in hot and in cold solution (Table II), it can be seen that there is, on the average, a difference in the volume of chromous sulfate consumed amounting to 0.29 per cent, a quantity too large to be disregarded in accurate quantitative work. Although this error could doubtless be compensated for by standardizing under the same conditions that prevail in an actual analysis, the objection would still remain that the reduction of iron by chromous sulfate in cold solution proceeds slowly in the vicinity of the end point.

It is well known that energetic reducing agents are oxidized, more or less rapidly, by the dissolved atmospheric oxygen in water, and this phenomenon might account for the greater volume of chromous sulfate that was used up when titrating a cold solution of ferric alum. Moreover, in those analyses in which the ferrous iron is oxidized by the careful addition of potassium permanganate prior to the reduction titration, the small excess of permanganate being destroyed by boiling, some of the dissolved oxygen is, in all probability, removed. Accordingly, titrations were performed on solutions of ferric ammonium sulfate that had been first boiled and then cooled down to room temperature by means of an ice bath while a current of carbon dioxide was passing through the liquid. The results, as shown in Table II, are slightly lower, the mean discrepancy being 0.10 per cent, than those previously obtained with cold solutions that had not been subjected to the preliminary treatment, yet noticeably higher than those obtained with hot solutions.

TABLE II. TITRATION OF CHROMOUS SULFATE AGAINST FERRIC ALUM

(20 cc. of ferric alum titrated in each experiment)

No.	CrSO ₄ (Fe SOLN. HOT) Cc.	CrSO ₄ (Fe SOLN. COLD) Cc.	CrSO ₄ (Fe SOLN. BOILED AND COOLED) Cc.
1	30.62	30.72	30.67
2	30.62	30.70	30.68
3	30.62	30.74	30.68
4	30.64	30.70	30.71
Av.	30.63	30.72	30.69

Thornton and Wood (9), when verifying the end point obtained by the use of potassium thiocyanate as indicator in the reduction of iron with titanous sulfate, found that the thiocyanate seemed to behave as a catalyst, thus expediting the reaction. Therefore, it was decided to ascertain whether or not the above-mentioned thiocyanate has a like effect in the titration of iron with chromous sulfate. For this purpose, 20 cc. of the ferric alum solution were diluted with 40 cc. of water, acidified with 12 cc. of sulfuric acid (1 to 1), and treated with 10 cc. of potassium thiocyanate (10 per cent solution). After sweeping with carbon dioxide for 10 minutes, the titration was conducted at the customary rate until the intense reddish color due to ferric thiocyanate had faded to an appreciable extent, whereupon the reducing agent was added slowly up to the point of complete reaction.

Throughout the entire series of experiments, wherein 10 cc. of the thiocyanate solution were used, the values seem to decrease with increase of temperature (Table III). Thornton

and Chapman (8) obtained similar indications when titrating with titanous chloride. Furthermore, a number of workers (7) have observed the bleaching of ferric thiocyanate in connection with the colorimetric determination of iron.

TABLE III. TITRATION OF CHROMOUS SULFATE AGAINST FERRIC ALUM

(20 cc. of ferric alum titrated in each experiment)					
No.	Room Temp. ^a ° C.	CrSO ₄ 1 cc.	CrSO ₄ 5 cc.	CrSO ₄ 10 cc.	CrSO ₄ 20 cc.
		Cc.	Cc.	Cc.	Cc.
1	19.6	30.69 ^b	...	30.72	...
2	19.7	30.67 ^b	...	30.70	...
3	20.0	30.67	...
4	20.0	30.68	...
5	20.5	30.72	...
6	20.6	30.67	...
7	20.9	30.70
8	21.0	30.71
9	21.3	30.67	30.70	30.70	30.73
10	21.6	30.65	...
11	22.0	30.62	...
12	22.2	30.54	...
13	22.8	30.51	...
14	26.7	30.70	30.55	30.37	30.27

^a Temperature of chromous sulfate solution.
^b Solution boiled and cooled to room temperature before adding thiocyanate.

Experiments were made with varying quantities of potassium thiocyanate present, and the results show that the amount of chromous sulfate required is influenced not only by the temperature but also by the concentration of the former reagent, there being a noteworthy diminution in the volume of the chromium solution accompanying an increment in the

solution was enough to cause the potential of the test solution to fall from the value corresponding to trivalent iron to the very low value corresponding to bivalent chromium (Figure 2).

As an additional means of testing the validity of the proposed method, determinations of iron in a sample of ferrous ammonium sulfate were made.

The iron value of the ferric alum solution was found to be 0.005706 gram per cubic centimeter by reducing two 25-cc. portions in the reductor according to the instructions of Lundell and Knowles (6, 11) and then titrating the ferrous salt with potassium permanganate, which in turn had been standardized against the certified sodium oxalate of the Bureau of Standards (Standard Sample No. 40). Taking the mean of the results obtained in experiments 1 and 2 of Table III, and correcting the volumes to the standard temperature, 20° C., and for the graduation errors of the measuring instruments, we find that 30.69 cc. of chromous sulfate were equivalent to 20.01 cc. of ferric alum. Therefore, 1 cc. of the chromous sulfate solution represented 0.0037203 gram of iron.

Judging from the experience of Thornton and Wood (9) it would seem that specimens of ferrous ammonium sulfate taken at random do not always contain the theoretical percentage of iron. Consequently, the c. p. salt was recrystallized in such a way as to procure a fine-grained, homogeneous material (9), and the iron content of the finished product was carefully determined by the reductor method. It was found to contain 14.30 per cent of iron instead of 14.24, as demanded by theory.

An accurately weighed portion of the Mohr's salt was dissolved in 40 cc. of water, 12 cc. of sulfuric acid (1 to 1) were added, and the ferrous iron was oxidized with 0.1 *N* potassium permanganate, care being taken not to overstep the end point. The solution was then boiled for 10 minutes to decompose the small excess of permanganate inevitably introduced, and the cooled liquid was titrated with chromous sulfate in the usual manner, 1 cc. of potassium thiocyanate (10 per cent solution) being added for its accelerating effect upon the reduction of the ferric salt. The potassium permanganate was tested for iron, but none was found.

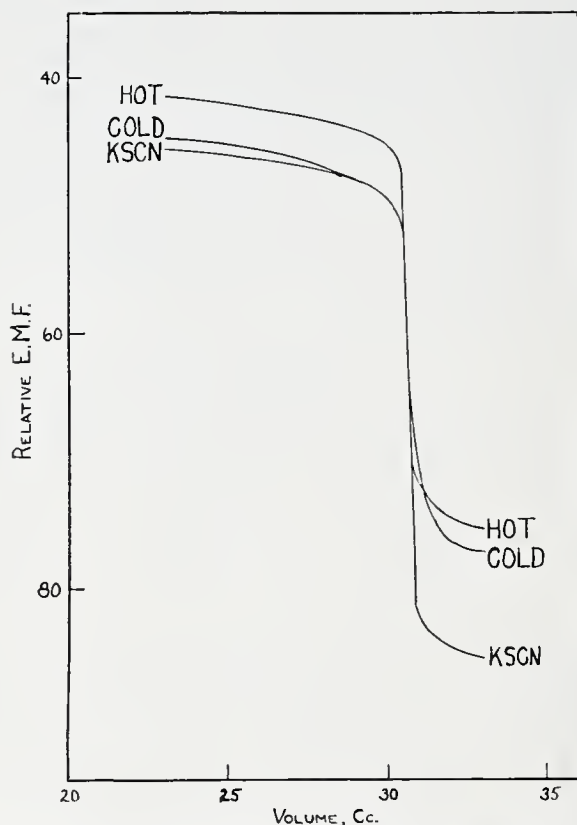


FIGURE 2. TITRATION CURVES OF CHROMOUS SULFATE AGAINST FERRIC ALUM

concentration of the thiocyanate at temperatures ranging above 22° C. When only 1 cc. of a 10 per cent solution of potassium thiocyanate was added, however, the result was not affected by a considerable rise of temperature; yet the reaction appeared to proceed just as rapidly as in the presence of much larger quantities of the salt. Besides, the change in potential was greater than that observed in either cold or hot solution in the absence of the accelerator. In fact, one drop (approximately 0.03 cc.) of the 0.067 *N* chromous sulfate

TABLE IV. TITRATION OF CHROMOUS SULFATE AGAINST FERROUS AMMONIUM SULFATE

No.	Mohr's Salt Taken	CrSO ₄ Required	Fe (By Reductor)	Fe Found	Diff.
	Grams	Cc.	Gram	Gram	Gram
1	0.8602	33.05	0.1230	0.1230	0.0000
2	0.5034	19.31	0.0720	0.0718	-0.0002
3	1.0509	40.36	0.1503	0.15015	-0.00015

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Microdetermination of Protein in Cereal Products

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MICROMETHODS of analysis were originally developed for use when only a small sample of the material could be obtained. More recently they have proved so accurate, rapid, and economical that they are now used in many determinations even when there is an abundance of sample available.

This paper deals with an adaptation of the microdetermination of nitrogen for usage in the cereal industries, just as Bermann (3) applied micromethods to the determination of nitrogen in the fermentation industry.

PROCEDURE

Using a microchemical balance, from 10 to 20 mg. of sample are weighed into a micro-Kjeldahl digestion tube. A small crystal of copper sulfate and 2 ml. of concentrated nitrogen-free sulfuric acid are then added. The sample is thoroughly mixed with the acid and then heated until the organic matter is charred. This usually requires about 4 minutes. A micro-Kjeldahl digestion rack is very convenient for use in this operation, since several samples may be digested at the same time. The digestion mixture is allowed to cool, after which 1 gram of potassium persulfate is added (?). The mixture must be cooled to at least 100° C., otherwise the potassium persulfate decomposes at the surface of the hot liquid, producing an inefficient oxidation. The mixture is again heated gently until complete decomposition of the potassium persulfate has taken place. A perfectly clear sample is usually obtained after heating approximately 1 minute, and the time for the entire digestion is usually less than 10 minutes. A distillation equipment similar in principle to that of Kemmerer and Hallett (4) was used for this investigation and gave accurate results, although it was not so suitable for routine work as their more elaborate apparatus.

The digested sample is washed into the distillation flask and sufficient 40 per cent carbonate-free sodium hydroxide solution added to neutralize the excess sulfuric acid. The ammonia is expelled by steam distillation, assisted by the heat from a microburner beneath the distillation flask. About 25 ml. of the distillate are collected in a known volume of *N*/70 sulfuric acid. The time required for distillation is from 5 to 8 minutes.

The back titration is made with *N*/70 carbonate-free sodium hydroxide solution, using methyl red as the indicator. Satisfactory results were obtained without first boiling the acid distillate as recommended by Pregl (6), or without cooling to 15° C. as specified by Allen and Davisson (1).

PRECAUTIONS

Distilled water should be freed from dissolved ammonia and carbon dioxide, or otherwise large errors would be incurred. With certain waters a satisfactory purification may only be accomplished by redistilling from an acid permanganate solution. However, it has been the authors' experience, using distilled water from a source originally containing very small quantities of impurities, that the freeing from ammonia and carbon dioxide was accomplished most easily by vigorous

boiling for several minutes. A metal container is required for this operation, since hot water extracts appreciable quantities of alkali from glass vessels, as shown by Walther (8). Distilled water containing alkali yields high nitrogen results, as it is used to dilute the acid in the ammonia-distillate receiver.

Pregl recommended that a fused quartz tube be used in the condenser to eliminate the possibility of the steam and hot water extracting alkali from the glass. In this investigation a Pyrex tube was used and very satisfactory results were obtained, indicating that the time of contact was insufficient to incur error. Blank determinations should be made from time to time and appropriate corrections applied if necessary.

EXPERIMENTAL RESULTS

To demonstrate the accuracy and practicability of the method, pure acetanilide was analyzed. The percentage of nitrogen found was 10.32, the theoretical value being 10.37. Results equally as satisfactory were obtained when using certain cereal products, as shown in Table I, the micro results being compared with those found by the Official Gunning Method (2).

TABLE I. COMPARISON OF MICRO- AND MACROMETHODS

SAMPLE	MATERIAL	MOISTURE %	PROTEIN (N × 5.7) BY:		
			Macro %	Micro %	Diff. %
1	Flour	12.5	11.74	11.73	-0.01
2	Flour	14.0	10.65	10.41	-0.24
3	Flour	13.4	14.84	14.41	-0.43
4	Flour	13.2	10.88	10.74	-0.14
5	Wheat	8.0	11.87	12.07	+0.20
6	Wheat	8.5	16.20	16.36	+0.16
7	Wheat	12.6	12.69	12.71	+0.02
8	Corn	10.6	7.81	7.68	-0.13

The wheat and corn samples were ground on a Wiley laboratory mill (9) so that the entire sample passed through a screen of 0.5-mm. mesh. Samples 1, 2, and 5 were collaborative samples of the Association of Pacific Northwest Cereal Chemists, and consequently the macro results reported for these samples represent the averages of the protein as determined by at least seventeen different laboratories. In the other cases the micro results are compared with those obtained by the authors using the Official Gunning Method.

On a routine basis an analysis can be made in about 35 minutes. The rapidity of this method for determining protein should be of great value to the cereal industries, inasmuch as it provides a means for rapidly checking their products.

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Determination of Uranium in Carnotite Ore

Glacial Acetic Acid Method

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SOME years ago the author (1) suggested the use of glacial acetic acid for the separation of uranium from vanadium with the subsequent precipitation of uranium with ammonium hydroxide and ignition to the oxide, U_3O_8 . In the recent investigation of this method a comparison was made with Low's method of the separation of vanadium as lead vanadate. The laboratory work was conducted by Marshall Hall Blain under the author's supervision.

The interfering substances in carnotite are silica, iron, aluminum, and vanadium. A synthetic mixture was made from carefully prepared reagents and the separations made according to the procedure outlined by the author (2). Separations of vanadium as lead vanadate, according to directions by Low, with subsequent determination of vanadium were also made on synthetic mixtures. The results are given in Tables I and II.

TABLE I. LEAD VANADATE METHOD OF LOW

PRESENT	FOUND				
	1	2	3	4	5
Gram	Gram	Gram	Gram	Gram	Gram
SiO ₂	0.2035	0.2026	0.2029	0.2025
Al ₂ O ₃	0.0717	0.0702	0.0706
Fe ₂ O ₃	0.1316	0.1305	0.1306
V ₂ O ₅	0.2166	0.2174	0.2178	0.2172
V ₃ O ₈	0.2521	0.2511	0.2506	0.2508	0.2505

TABLE II. GLACIAL ACETIC ACID METHOD OF SCOTT

PRESENT	FOUND				
	1	2	3	4	5
Gram	Gram	Gram	Gram	Gram	Gram
SiO ₂	0.2035	0.2013	0.2017	0.2021
Al ₂ O ₃	0.0717	0.0706	0.0709
Fe ₂ O ₃	0.1316	0.1304	0.1307
V ₂ O ₅	0.2166	0.2143	0.2156	0.2171	0.2152
U ₃ O ₈	0.2521	0.2514	0.2517	0.2530	0.2515

The low results by the lead vanadate method are due, possibly, to the occlusion of uranium by lead vanadate. The separation of vanadium from uranium by this method takes a longer time than the glacial acetic acid separation. The following observations were made regarding the details of the glacial acetic acid method:

1. In the carbonate extraction of uranium the solution should be boiled at least 30 minutes or, if preferred, the solution may be taken to dryness and gently baked to ensure removal of carbon dioxide.

2. Hydrochloric acid may be used in place of nitric acid for neutralization of the solutions.

3. Iron and aluminum should be precipitated from cold solution.

4. When testing the acetic-nitric extract for the presence of vanadium, the addition of a drop of hydrochloric acid intensifies the reddish brown color produced by hydrogen peroxide.

5. Enough ammonium salts are generally present in the solution in which the ammonium uranate is to be precipitated to facilitate the precipitation without the addition of more.

6. The uranium should be precipitated from a hot solution by the addition of ammonium hydroxide, drop by drop, with constant stirring.

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Apparatus for Calibration of Flowmeters

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A METHOD for the calibration of flowmeters of the resistance-tube type for use with small rates of gas flow is herein described. Its principal advantages are the following: ease and rapidity of operation; the fact that the flow of gas is in no way disturbed during the measurement; and the fact that the head of water against which the gas flows is practically zero at all times, thus ensuring greater accuracy by excluding the "siphon effect" in the delivery tube from *E* to *F* (see Figure 1).

The gas with which the meter is to be used is introduced into the apparatus under pressure from the gasometer or other container in which it is stored. *B* is a 2-liter Wolff bottle which is to relieve any slight fluctuations in the gas flow. *C* is the flowmeter. *D* is an empty balloon flask of about 2-liter capacity, and is fitted with a three-hole rubber stopper. The valve, *a*, is opened and closed by means of a screw clamp.

E is another 2-liter balloon flask containing water, and is fitted with a rubber stopper through which pass the delivery tube from *D*, the delivery tube from the aspirator bottle, *A*, which is used as a storage reservoir for water, and the delivery tube through which the water is displaced by the gas. *F* is a specially constructed pipet with a volume of 100 cc. between two marks above and below the bulb, respectively. The

lower end of the pipet may be closed by the screw clamp valve, *c*.

To perform the calibration, water is run into *E* from *A* by opening the stopcock *b*. The water level should be slightly above the level of the pipet end of the delivery tube, as shown at *x*, so that this tube will not act as a siphon during the process.

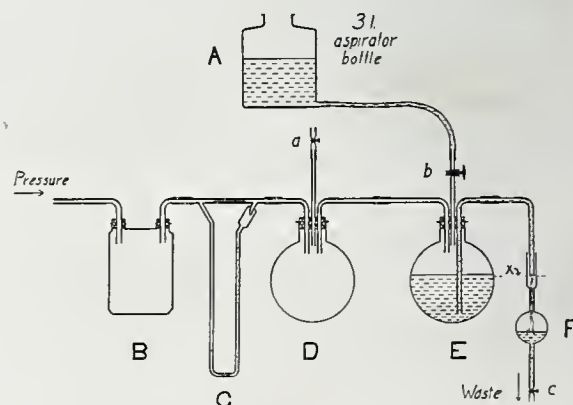


FIGURE 1. APPARATUS FOR CALIBRATION OF FLOWMETERS

Stopcock *b* is then closed, and clamp *a* is closed. The pipet is left open at *c* at first. The gas flow is then begun, and water flows through the open pipet for a few seconds to allow the flow to become steady. The reading of the meter is noted, and immediately *c* is closed and the time required by the water to fill the pipet between the two marks is observed with a stopwatch. Three or four check runs should be made without changing the rate of flow. The water level must be kept the same always by letting water run in from the aspirator bottle

when necessary. For greatest accuracy, this should be done before each reading. Since the flask *E* is large, there will be little change in water level during each measurement.

Four or five different flow rates should be determined in this manner. Then, plotting the rates of flow in cubic centimeters per minute against the meter readings, a curve may be constructed from which any desired data may be read directly.

RECEIVED November 6, 1931.

A New Colorimetric Test for Chromium

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WHILE searching for methods of determining minute quantities of chromium, the writer recalled a dyeing technic in which woolen fiber colored with certain acid dyestuffs is given a subsequent treatment in a bath containing potassium dichromate and sulfuric acid. In many cases this after-chroming effects a distinct color change on the woolen fabric and greatly increases the fastness of the color.

This technic suggested a possible method for the detection of small quantities of chromium by warming previously dyed wool samples in acid solutions that were known or believed to contain chromic acid. Preliminary experiments were accordingly made on woolen yarn that had been dyed with 1 per cent of serichrome blue R (1, 2) with results which justified further experimentation. This dyestuff, serichrome blue R, despite its name, imparts to wool a bright crimson color with a faint bluish tinge. The deep navy blue shade of the finished wool is developed by chromic acid in the second bath. No other dyestuff seemed to offer any advantages over this for analytical purposes. It is possible that some other dye would be better for quantitative results.

For this work wool flock (finely ground wool) was used, although woolen yarn may be used if preferred. The dyestuff solution was made by dissolving 100 mg. of serichrome blue R in water and making up to 200 cc.

The dyeing operations used were the following:

To a 125-cc. Erlenmeyer flask were added 40 cc. of water, 0.1 gram of sodium sulfate, and 0.02 gram of sulfuric acid. (The quantities of sodium sulfate and sulfuric acid added represent 5 per cent and 1 per cent, respectively, of the weight of the wool taken.) Two grams of the wool were added and the flask was shaken to ensure thorough wetting of the fiber. The desired quantity of dyestuff was then added (0.5 per cent is recommended—i. e., 20 cc. of the solution). The mixture was stirred well and heated at full temperature of the steam bath for 30 minutes, after which it was filtered on paper by suction in a Büchner funnel, washed free of acid, and dried.

The color standards were prepared as follows: A standard chromium solution was made by dissolving 0.282 gram of potassium dichromate in water and making up to a volume of 100 cc. (1 cc. of this solution contains 1 mg. of chromium as Cr.) From this solution a working standard containing 0.01 mg. of chromium in each cubic centimeter was made.

To each of ten beakers were added 50 cc. of water, 3 cc. of 1 N sulfuric acid (not standardized), and 0.1 gram of wool previously dyed with serichrome blue R. The mixture was stirred to ensure thorough wetting of the fiber and such quantities of the potassium dichromate solution as represented from 0.01 mg. to 0.1 mg. of chromium were added to the respective beakers, which were then covered with watch glasses. The mixture was heated on a steam bath at full temperature from 20 to 30 minutes with occasional stirring, filtered by suction on paper (small Büchner), washed, dried,

and mounted on a spot plate in Duco household cement thinned down with an equal quantity of amyl acetate. The wool samples thus treated were found to have developed a blue shade in proportion to the amount of chromium which acted on the dyed sample.

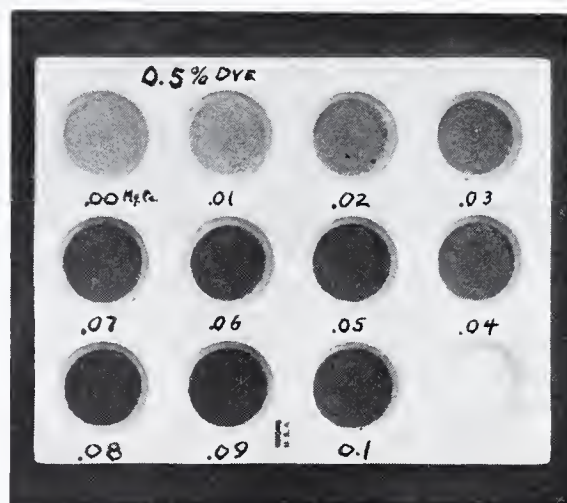


FIGURE 1. CHROMIC ACID DEVELOPMENTS IN SERICHROME BLUE R

To test for chromium in unknown samples, separate the chromium, ferric iron, and aluminum in the form of hydroxides. Filter by suction in a Gooch crucible provided with an asbestos mat (preferably on a removable disk) and wash with water. Remove the asbestos with the precipitate to a beaker and add 30 cc. of water and 3 cc. of normal sodium hydroxide solution. Mix well and add 5 cc. of hydrogen peroxide solution (U. S. P.). Allow to stand about 30 minutes, and then warm on a steam bath until hydrogen peroxide is decomposed. Filter by suction and acidify the filtrate with 3 cc. excess of normal sulfuric acid, add with stirring 0.1 gram of dyed wool, and heat the covered beaker on the steam bath from 20 to 30 minutes. Filter by suction on paper, wash, and dry.

The presence of chromium is indicated by the development of a blue shade on the red fiber. If this color is not too dark the quantity of chromium may be estimated by comparison with the chromium color standards described above.

Confirmation of the method as here presented was made by comparing the colors developed by potassium dichromate solutions with those produced by chromic chloride solutions after oxidation. Both solutions, potassium dichromate and chromic chloride (solution A), were adjusted to contain 0.01 mg. of chromium in 1 cc. The first color standards represented 0.05, 0.07, 0.10, and 0.12 mg. of chromium respectively, besides a blank. In the first case chromic chloride

alone was used, in the second case the chromium solutions contained an admixture of ferric alum and alum. Fair duplication of solution A colors with those made by potassium dichromate was observed in all cases. More complete tests were then made using solution A in amounts that varied from 0.01 to 0.10 mg. of chromium, with checks that were invariably satisfactory. These results confirmed a number of tests that were obtained in earlier experiments in which potassium permanganate was used as an oxidizing agent instead of hydrogen peroxide.

Photographs of these chromium blue developments are readily distinguished from one another, as may be observed in Figure 1. In making these photographs the range of chromium color distinctions was materially extended by the use of light screens.

It is also of interest to note that chromium-developed wool samples may be stripped of their red color by warming with

dilute alkali solution (0.1 *N* sodium carbonate) without removing the chromium stain. These stains are proportional to the quantity of chromium present.

In order to ascertain if the color development herein described is characteristic of chromic acid, parallel experiments were tried on woolen yarn dyed with serichrome blue R using the following acids and salts in amounts equivalent to 1 mg. of metallic chromium: molybdic, tungstic, vanadic, and permanganic acids; also ferrous sulfate, manganous sulfate, and chrome alum. No change in color was observed.

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Separation and Determination of Calcium and Magnesium

8-Hydroxyquinoline-Saccharate Method

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SHEAD and Heinrich (2) reported a method for separating and determining calcium and magnesium in magnesian limestones and dolomites low in silica and iron, which consists in burning the rock to a mixture of the oxides of calcium and magnesium followed by extraction of soluble calcium oxide from insoluble magnesium oxide by a 30 per cent cane sugar solution. The residual magnesia is then titrated after filtration and the mixed oxides are obtained by a titration of the original limestone. From these data rapid and accurate determinations of calcium and magnesium can be obtained. The method is restricted in its application because, if silica is present, calcium silicates insoluble in sugar solutions are formed, and hence a separation of calcium and magnesium is impossible. To obviate these difficulties and to extend the method over a wider range of applications, the 8-hydroxy-quinoline-saccharate method was devised for the separation of the two oxides, leaving the determination by titration substantially as described in the paper cited.

Silica and oxides of iron and aluminum are removed from a weighed sample in the usual way, as are also interfering heavy metals, if present. From the hot filtrate, calcium as oxalate and magnesium as 8-hydroxyquinolate (1) are precipitated together by the addition of the calculated amount of 8-hydroxyquinoline dissolved in the required quantity of a hot solution of oxalic acid previously saturated in the cold. The calcium precipitates first from the slightly acid solution. The solution is then gradually made alkaline with ammonium hydroxide until about 10 per cent by volume has been added, and allowed to stand until precipitation is complete (an hour or two). The mixed precipitate is filtered off on paper and washed with 2 to 5 per cent ammonium hydroxide, ignited to the mixed oxides in a porcelain crucible containing a piece of platinum foil, and weighed. In case the material under examination is a limestone or dolomite, the weighing as mixed oxides can be omitted, as it is much more convenient to obtain these data by a titration of the unburned limestone which seldom carries such impurities as would vitiate the alkalimetric titration. The freshly ignited mixed oxides are then extracted with 30 per cent saccharate solution (2). The extraction and washing of the residual insoluble magnesia

are rapid provided that treatment at this point is prompt, as standing admits of the hydration of magnesium oxide to magnesium hydroxide which is colloidal in nature. Filtration of magnesium oxide is rapid and hence the solution needs no protection from carbon dioxide in the air. If magnesium hydroxide is formed, additional apparatus is required to exclude the carbon dioxide. The extraction and washing should not require more than 15 to 20 minutes, as the solution of freshly ignited calcium oxide is rapid and the mixture is not an intimate one because the bulk of the calcium is precipitated out in slightly acid solution before the magnesia precipitates in the strongly alkaline environment.

The method as reported in this and the preceding paper (2) is both rapid and accurate in the hands of a competent chemist. Table I presents some representative results.

TABLE I. REPRESENTATIVE RESULTS FOR CALCIUM AND MAGNESIUM OXIDE IN DOLOMITIC LIMESTONES

SAMPLE	WT. SAMPLE Gram	MIXED OXIDES Gram	0.3479 <i>N</i> HCl FOR	0.1256 <i>N</i> NaOH FOR	MgO %	CaO %
			MgO Cc.	FOR MgO Cc.		
1	0.2178	0.1055	15.0	36.1	6.33	42.10
1 (Av. of 6)	0.2178	0.1053	15.0	36.3	6.22	42.12
1 (By gravimetric methods)					6.38	42.00
2	0.2339	0.1291	15.0	36.1	5.89	49.29
2 (Av. of 6)	0.2339	0.1292	15.0	36.2	5.87	49.37
2 (By gravimetric methods)					5.86	49.19
3	0.2724	0.1428	15.0	37.4	3.85	48.57
3 (Av. of 6)	0.2724	0.1431	15.0	37.4	3.83	48.73
3 (By gravimetric methods)					3.81	48.46
4	0.2247	0.1170	25.0	51.4	20.11	31.95
4 (Av. of 6)	0.2247	0.1171	25.0	51.4	20.14	31.97
4 (By gravimetric methods)					20.08	31.96
5	0.9910	0.5173	60.0 (0.2 <i>N</i>)	13.5 (0.0915 <i>N</i>)	21.89	30.31
5	0.73885	0.3869	60.0 (0.2 <i>N</i>)	44.25 (0.0915 <i>N</i>)	21.69	30.67
5	0.7369	0.3857	60.0 (0.2 <i>N</i>)	43.25 (0.0915 <i>N</i>)	22.00	30.34
5 (Av.)					21.86	30.44
5 (B. S. Dolomite 88)					21.48	30.48

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HARRISON E. HOWE, EDITOR

Estimation of Small Amounts of Iron in Copper

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SOME time ago the author was requested to determine the percentage of iron in some copper in the form of turnings which appeared clean, bright, and free from dust and oil. Ten-gram samples were dissolved in nitric acid, the solutions neutralized with ammonium hydroxide, and a slight excess added. The solutions were boiled, allowed to stand on a hot plate for several hours, the precipitated ferric hydroxide was filtered out, washed, and dissolved in dilute hydrochloric acid (1 to 15), and, after the addition of 5 cc. of bromine water, reprecipitated with ammonium hydroxide and washed free from copper. The precipitates were again dissolved in dilute hydrochloric acid, and the iron was estimated by the salicylic acid colorimetric method described by Yoe (1), which consists essentially of adding salicylic acid to a neutral solution of ferric iron and comparing the color with that of a standard sample treated in the same way.

The results were very discordant. In six runs the percentages were 0.0045, 0.0065, 0.0031, 0.0049, 0.0035, and 0.0039. No trouble was experienced in checking the colorimeter readings against standard solutions containing approximately the same amount of iron.

The estimation of minute amounts of such a widespread element as iron requires special precautions to avoid contamination from outside sources. The beakers, funnels, etc., used were thoroughly cleaned and then boiled out with concentrated hydrochloric acid and washed with distilled water. Blanks were run and corrections were made, where necessary, for the iron present in the reagents.

An investigation of other possible causes of such erratic results showed that most of the iron was on the copper and not in it.

Two hundred grams of turnings were treated with 500 cc. of water and 50 cc. of hydrochloric acid in the cold for about 2 hours. The turnings were filtered off and washed free from acid. A very little copper dissolved during the treatment, approximately 0.5 gram. Iron was determined in the filtrate. One 200-gram sample gave 0.0046 and another gave 0.0066 per cent iron. (All results are based on the weight of copper.) Duplicate 10-gram samples of the acid-washed copper were treated as before, and the iron found in the acid-washed turnings was 0.00086 and 0.00084 per cent, a satisfactory check.

The manner of contamination of the surface was next investigated. The cutting tool offered a possible source of

contamination and, in order to determine whether or not an appreciable amount of iron rubs off and contaminates the sample, the following experiment was performed.

A piece of copper wire bar was cleaned and placed on a clean lathe. The outside layer, about one-eighth inch (0.32 cm.) was turned off with a stellite cutting tool and discarded. A sample was turned off with the stellite tool and caught on a clean piece of paper. Then a sample was cut with a regular high-speed steel tool. Stellite was employed again, the two tools were alternated until about 3 pounds (1.36 kg.) of turnings had been collected. Each time the stellite was used a small amount of surface was turned off and discarded before starting to collect turnings. In this manner two samples were obtained from the same wire bar, one cut with stellite and the other with high-speed steel.

Two hundred grams of each sample were treated with dilute hydrochloric acid, as previously described. The first washing from the high-speed steel turnings yielded 0.00016 per cent iron, and those from the stellite turnings only 0.00006 per cent.

The samples were treated with another wash of 500 cc. of water and 50 cc. of hydrochloric acid, and after standing for 2 hours this was removed and a third wash put on them. Iron was estimated in each of the wash solutions. In both the second and third washings the amount of iron found was too small to allow comparison in a colorimeter, but was estimated to be about 0.00001 per cent. This corresponded to the amount found by running a blank on the hydrochloric acid. The first washing, therefore, must have removed all of the iron on the surface of the copper.

Fifty-gram samples of the washed and unwashed turnings were dissolved in nitric acid, and the iron determined as before, with the following results:

Stellite unwashed	0.00069%	High-speed steel unwashed	0.00080%
Stellite washed	0.00063%	High-speed steel washed	0.00063%

The source of the iron in the washings from the stellite turnings is not apparent. The stellite itself contained very little iron, less than 5 per cent. With copper in the form of turnings, a fairly large surface is exposed, and a small amount of the iron in the copper undoubtedly dissolves in the hydrochloric acid wash. This could hardly be 10 per cent of the iron present in the copper, however. Even though pains were taken to prevent incidental contamination, the author is

inclined to think this the most probable source of the greater part of the iron found in the washings.

Whether or not the cutting tool plays an important part in adding iron to the sample depends upon the extent of contamination from other sources. The following results, obtained from analysis of a piece of blister copper, serve as an illustration:

NATURE OF SAMPLE	IRON	
	Unwashed	Washed
	%	%
Surface turnings, stellite	0.035 ^a	0.00074
Inside turnings, stellite	0.0016	0.00083
Inside turnings, high-speed steel	0.0019	0.00083
Washings from inside high-speed steel turnings		0.00104
Washings from inside stellite turnings		0.00077

^a Weighed as Fe₂O₃.

Here again the washings from the steel-cut sample yielded more iron than those from the one cut with stellite. The amount, however, is so small in comparison with the difference between the percentages found in the washed and unwashed turnings as to be negligible.

The above results indicate that it is advisable to wash samples of copper with dilute hydrochloric acid when an accurate determination of iron is desired.

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RECEIVED November 10, 1930.

Specification of Color on Dyed Fabrics by Spectroanalysis

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THE files of a textile manufacturer contain many thousands of samples of dyed fabrics, either retained as standards for color lines or in connection with dyeing formulas which they illustrate. As standards for commercial production, such samples are frequently open to suspicion of having become soiled or faded, and a permanent record of the original condition of a sample would prevent occasional disputes from this cause. Since commercial matches usually deviate in some degree from the standard, some numerical measure of the discrepancies would be of great value in establishing tolerances. Moreover, a numerical record defining a color should be of value in systematic filing of the samples.

A spectrophotometric analysis of the light reflected from the colored sample is to the physicist the most satisfactory record and definition of the appearance of the sample. Whether the interpretation and use of such data by a textile manufacturer would be practicable has been open to question, but the time-consuming and expensive methods of color analysis which until recently were the only ones available prohibited any extensive practical trials. The invention of automatic recording color analyzers, notably one by Professor Arthur C. Hardy at Massachusetts Institute of Technology, subsequently developed and marketed by the General Electric Company, has radically simplified the task of preparing the spectrophotometric curves.

The purpose of this paper is to describe the experience at the laboratory of Cheney Brothers in recording the colors of fabric samples in terms of spectrophotometric curves using the General Electric recording color analyzer with modifications noted below.

The recording color analyzer has been described elsewhere by Hardy (2), and a general description will not be repeated. The machine, as delivered to Cheney Brothers' laboratory in January, 1930, was arranged to view an area of the sample about 1 mm. wide and 18 mm. long. The sample was held in a fixed position. It was found at once that this band of

By a modification of its sample holder, the General Electric recording color analyzer has been made applicable to analysis of color on fabrics. A program of work for applying spectroanalysis to color on fabrics is described, covering recording of color produced by individual dyestuffs, standard color lines, commercial matches, loss of color during fastness tests, and calculation of dye formulas.

illumination was too narrow to give a representative view of a fabric sample, for marked shifts in the recorded curve occurred with changes in the position of the sample. This was particularly serious in a fabric with a distinct rib effect such as a bengaline, but it was found that even in comparatively smooth weaves the surface irregularities were sufficient

to cause noticeable shifts in the position of the curve corresponding to changes in brightness with slight rotary shifts in the position of the sample in the sample holder. The manufacturer changed the optical system so as to increase the width of the area illuminated to approximately 3 mm., effecting some improvement. There still remained difficulty in obtaining reproducible readings because of vertical shifts in the curve resulting from slight rotation of the sample when replaced in the holder. Figure 1 illustrates the curves obtained from a sample of fabric when viewed in two positions 90 degrees apart. In the case of a satin this difference has been observed to be as much as 55 per cent.

ROTARY SAMPLE HOLDER

Following a preliminary demonstration of an experimental rotary sample holder by the General Electric Company, an inexpensive sample holder of this type was constructed and has proved highly satisfactory. Its construction is shown in Figure 2. A circular sample of fabric about 25 mm. in diameter is cut out with a die and placed behind a glass window in the holder which is mounted on the end of the shaft of a small motor. To correct for possible error due to viewing the sample through glass, the magnesium carbonate standard is cut in the shape of a thin disk which may be slipped into the sample holder behind the same glass window. The motor is so mounted in the cabinet of the color analyzer that the light strikes the sample at 90 degrees and is taken off at 45 degrees exactly as in the original fixed sample holder, the only difference being that the sample is rotated continuously. Experiments showed that the speed of rotation may vary over a wide range, and it is only necessary to avoid certain critical speeds at which synchronism with the flicker

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wheel occurs and a stroboscopic effect results. When this occurs, it is at once evident from the motion of the recording pen and can be stopped by a change in speed of the motor. A rheostat is installed in the motor circuit for this purpose. Motor speeds between 3000 and 10,000 r. p. m. were tried, and the lower speeds were found satisfactory.

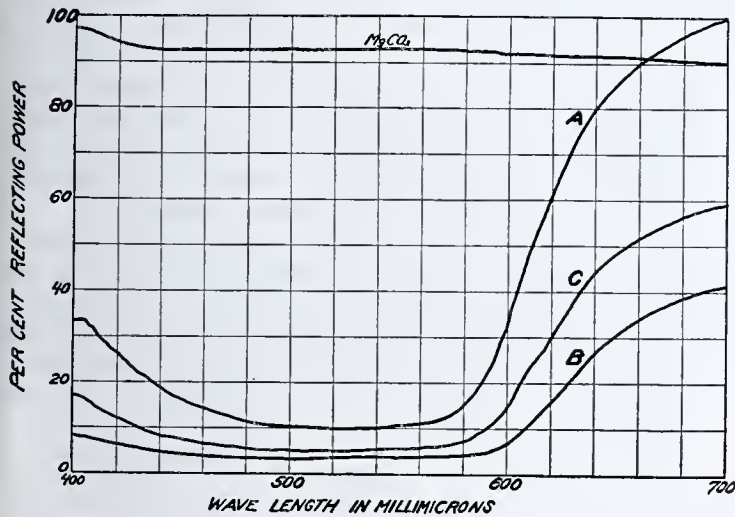


FIGURE 1. CURVES FOR A SAMPLE VIEWED IN TWO POSITIONS 90 DEGREES APART

- A. Warp vertical in stationary sample holder
- B. Warp horizontal in stationary sample holder
- C. Sample rotated

Referring again to Figure 1, there is shown the curve for a rotated sample as compared with curves obtained for the same sample viewed in two fixed positions 90 degrees apart. Figure 3 shows curves of samples of a satin and a crepe which were taken from goods accepted as a commercial color match. These illustrate the difficulty of comparing curves obtained with samples held in a fixed position and the good agreement of curves obtained from rotating samples. This confirms our assumption that the practical color matcher, when called upon to match fabrics of strikingly different construction, consciously or unconsciously matches the average appearance of one sample to that of the other with practically the result obtained by rotation in the color analyzer.

CALIBRATION OF COLOR ANALYZER

The color analyzer is calibrated and its correct adjustment is checked not only by running curves for magnesium carbonate, but by transmission curves for two glasses of known transmission values, one blue and one red. It has been the practice to make these tests once a day, keeping a permanent file of the curves obtained. All measurements made upon samples submitted are dated so that they may at any time be compared with the calibration curves for that day. Ex-

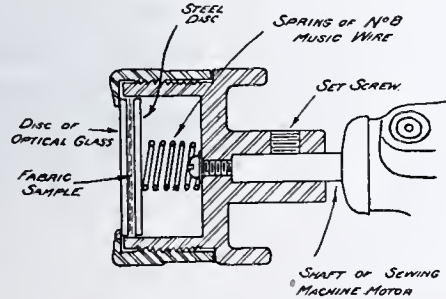


FIGURE 2. ROTATING SAMPLE HOLDER

perience has shown that the calibration curves do not shift appreciably during any one day, so it has not been necessary to run them for each fabric sample tested. For convenience in subsequent calculations, the curve for magnesium carbonate is generally recorded on the sheet with those of samples analyzed.

PREPARATION OF FABRIC SAMPLES

It will be appreciated that satisfactory results depend not only upon the performance of the color analyzer but also upon the preparation of the sample. In trying to define a dyestuff, not in terms of a sample of the dyestuff as obtained from the manufacturer but in terms of its color value when applied to a sample of fabric, the dyeing technic is exceedingly important. In dyeing silk, perfect exhaustion does not usually occur in the laboratory and is seldom obtained in plant practice. Reproducibility of dyeings depends, therefore, upon exceedingly accurate standardization of the dye-bath and the whole procedure for dyeing.

In spite of marked improvement in dyeing technic acquired through the necessity for reproducibility and the evidence shown by the color analyzer of frequent deviations in dyeing uniformity, it is believed that at present the limiting factor in accuracy in these experiments is in application of the dyestuffs to the fabric rather than in the measurements obtained with the color analyzer. It is safe to say that one by-product of real value from the experience in this laboratory

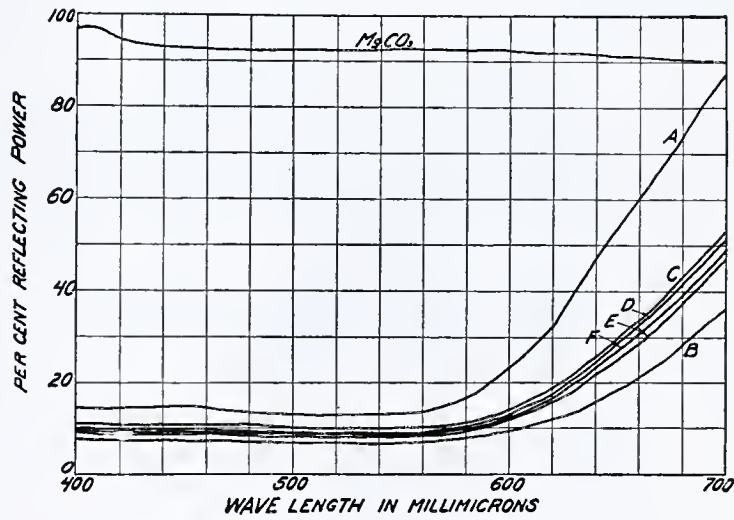


FIGURE 3. COMPARISON OF COLORS ON SATIN AND CREPE SILKS

- A. Satin with warp vertical
- B. Satin with warp horizontal
- C. Satin rotated
- D. Crepe with warp vertical
- E. Crepe with warp horizontal
- F. Crepe rotated

with the color analyzer has been the growth of a consciousness of the possibility of more exact reproduction of dyeings and a resulting general improvement in laboratory practice.

In the case of samples of fabrics obtained from mill production or from outside trade, there has been a limitation in the application of the color analyzer owing to the area of sample required for examination. Not only is a circular sample 25 mm. in diameter used in the present sample holder, but several thicknesses of the material have been necessary to avoid errors due to the light passing through the sample. In the case of thin goods such as voiles, as many as sixteen thicknesses have been found necessary, although in most fabrics three or four layers are sufficient. Printed designs seldom offer large enough areas of a given color to furnish the necessary samples. In piece dyed goods there is no trouble provided sufficient material has been submitted for test.

At the time of this publication, although some measurements of color on yarn samples have been made, a completely satisfactory method of mounting the yarn sample has not been developed. The construction of the sample holder made it convenient to pack the space behind the glass with small bits of fiber clipped from the sample, but it was demonstrated that the curve obtained varied with the fineness of cutting of the yarn, and a more representative curve would be had if all the yarn fibers could be stretched smooth and flat behind the glass of the sample holder. With a larger sample holder

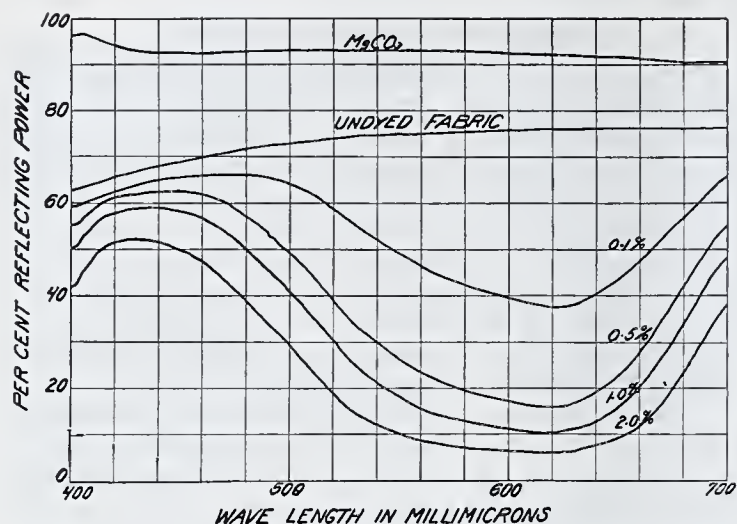


FIGURE 4. FAMILY OF CURVES FOR BRILLIANT WOOL BLUE FFR APPLIED ON SILK CREPE

in which a square card could be mounted, this condition could readily be obtained using several layers of yarn wound around the card.

APPLICATION IN PLANT CONTROL

Having obtained results with the color analyzer which indicated that under certain conditions significant curves could be obtained from fabric samples, the following outline was made as a program of work for establishing the use of the color analyzer in control testing in textile manufacture:

- I. Records of individual dyestuffs
 - a. To assist in controlling quality of dyes purchased
 - b. To furnish data for calculation of dye formulas
- II. Records of regular color lines

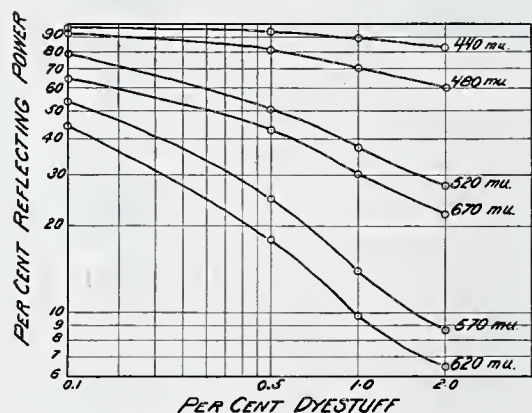


FIGURE 5. DATA FOR BRILLIANT WOOL BLUE FFR REPLOTED FROM CURVES OF FIGURE 4 AFTER CORRECTING FOR MAGNESIUM CARBONATE AS 100 PER CENT REFLECTION AND FOR COLOR FROM UNDYED FABRIC

- III. Records of matches obtained in commercial production
 - a. To accumulate data for tolerances in deviations from standard color lines
- IV. Records of wash tests and light tests on individual dyestuffs and standard color lines
 - a. To accumulate data on which to establish tolerances for loss of color during these tests
- V. Calculation of formulas in terms of two or more dyestuffs required to produce a color on fabric from which a given spectrophotometric curve will be obtained

I. RECORDS OF INDIVIDUAL DYES

For this purpose dyeings were made on a crepe fabric with each of the commonly used dyestuffs. Dyeings were made in each case with a series of percentages of dye (calculated, as is customary in dyeing practice, on the weight of the fabric sample). The values taken were 0.1, 0.5, 1.0, 2.0, and 4.0

per cent. Of this series the 2.0 per cent dyeing was chosen as a standard of comparison for shipment testing.

As a rule, a shipment of dyestuff which is within 5 per cent of the concentration guaranteed by the manufacturer is satisfactory provided the hue is correct. The increasing application of standardized dyeing in which a definite dyeing formula is supplied the dyehouse by the laboratory has made it necessary to keep strictly within these limits, a shipment of higher concentration being just as objectionable as one of lower concentration. Thus far, in shipment-testing, judgment has been passed first by the eye, and only those shipments which seem questionable have been tested further on the color analyzer to attempt to evaluate the exact percentage deviation or to prove a discrepancy in hue.

As mentioned above, curves were obtained for a given dyestuff at a series of different percentage dyeings, all being recorded upon one sheet of paper as illustrated in Figure 4. Since the light absorbed by the dyed sample is proportional (over a limited range of concentrations) to the logarithm of the concentration of dyestuff taken up by the fabric, it is con-

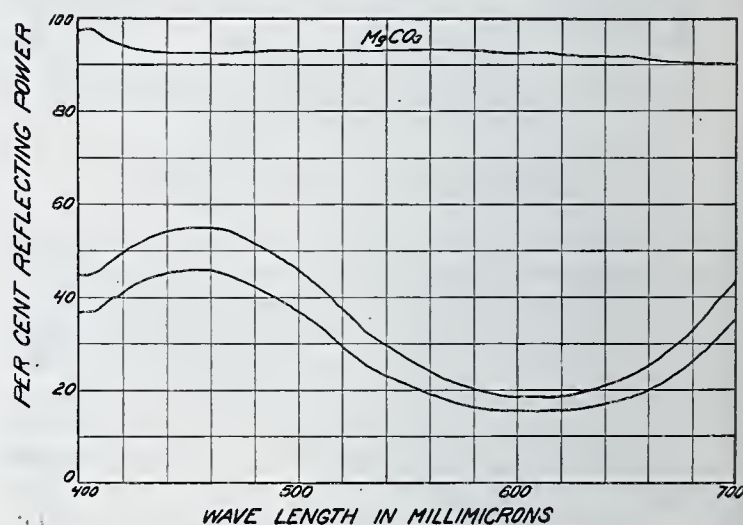


FIGURE 6. CURVES OF TWO SAMPLES OF POOR MATCH WITH DIFFERENCE IN BRIGHTNESS, NOT HUE

venient for purposes of interpolation to plot this data over on another sheet as illustrated in Figure 5. In order to include the range of values most conveniently, log concentration has been plotted against log reflection. In Figure 5 each curve represents the reflection at any concentration at a given wave length. The curves thus obtained are used in interpreting deviations in color-analyzer curves in terms of per cent dyestuff involved, applying both in estimations on faulty shipments of dyes and in calculation of dye formulas to correspond to given spectrophotometric curves.

II. RECORDS OF REGULAR COLOR LINES

The collection and filing of curves for all colors offered for sale in the various fabrics is largely a routine type of test. This is being done for current production, and the resulting curves serve as permanent records and as standards with which questionable matches from commercial production may be compared. The authors have postponed trying to develop a filing system based on values to be derived from these curves, feeling that this can be undertaken most conveniently when a large number of measured samples has been collected. The simplest system to suggest itself consists of designating each color by a number derived from the ordinates of the curve at a number of arbitrarily chosen wave lengths. (The present practice is to designate colors in the manufactured line by numbers which have no significance whatever.) A numerical expression in terms of three excitation factors calculated from the curve would be still more sig-

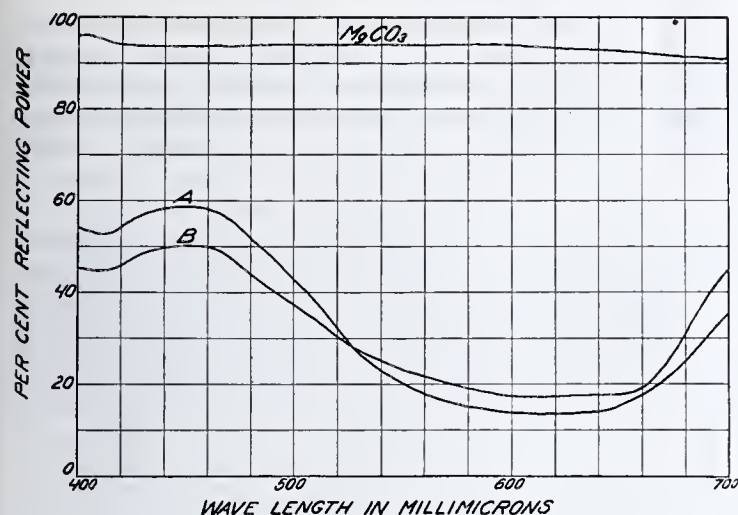


FIGURE 7. CURVES OF TWO SAMPLES POORLY MATCHED BECAUSE OF HUE

PHYSIOLOGICAL STIMULI CALCD. FROM O. S. A. EXCITATION FACTORS

	VIOLET	GREEN	RED
A.	228561	63599	47940
B.	192284	65150	54366
Diff., %	15.9	2.4	13.4

nificant but, as is pointed out later, the calculation involved is somewhat slow and tedious.

III. COMMERCIAL MATCHES

For a time analyses were made of samples obtained from each dye lot in commercial production and compared with the standard sample each was intended to match. In the case of 130 consecutive dye lots, only one lot had been criticized as off-shade by the regular inspectors, and curves obtained with the color analyzer indicated only one lot aside from this one to be very questionable. Since records of poor matches were more useful than those of satisfactory lots because the data were to be used for correlation between the discrepancies in the curves obtained by the color analyzer and the opinion of the regular inspectors on poor matches, it was necessary to dye up in the laboratory a series of approximately matched samples varying in exactness of match and have them classified by the inspectors.

It was also necessary to supply some simple numerical expression for the difference between two curves. When the two curves are practically parallel, as is the case in Figure 6, the difference is one of brightness only and may be expressed in terms of the difference in per cent of reflection at some one wave length, or, if preferred, in terms of the difference in area beneath the two curves.

Blue					Green					Red				
Reading	Factor	Sensation	S	M	Reading	Factor	Sensation	S	M	Reading	Factor	Sensation	S	M
400 S	47	253	11890		440 S		7			480 S		14		
M	40.5			10230	M					M				
420 S	52.6	614	22400		460 S		38		2160	500 S		34		3360
M	45.0			17550	M					M				
440 S	58.2	1019	39350		480 S		122		6100	520 S		233		6300
M	52			29990	M					M				
460 S	67	1442	49000		500 S		260		10520	540 S		373		7950
M	62.5			39000	M					M				
480 S	80	2073	63600		520 S		510		12800	560 S		466		7220
M	74.1			48560	M					M				
500 S	90.4	323	7280		540 S		603		15000	580 S		520		7045
M	82.9			4460	M					M				
520 S	107	471	1270		560 S		578		12550	600 S		510		6670
M	97			1647	M					M				
540 S	120	59	370		580 S		12.5		5800	620 S		375		4070
M	107			637	M					M				
560 S	135	11	171		600 S		196		2500	640 S		195		2630
M	119			209	M					M				
Total			228561	192284	Total			63599	65150	Total			47940	54366
Deviation from Std.			15.9%		Deviation from Std.			2.4%		Deviation from standard			13.4%	

S= Standard sample
M= Sample to be compared

FIGURE 8. FORM USED FOR CALCULATION OF EXCITATION VALUES

When the discrepancy is due to hue difference, it cannot be expressed so conveniently. A typical case is shown in Figure 7. Here it is necessary to follow the procedure of multiplying successive ordinates along the curve by the values at corresponding wave lengths for each of the three curves for the excitation factors, as established by the Optical Society of America (3), and obtaining three new curves, the areas under which may be represented by simple numbers. This is a tedious procedure, requiring from one-half hour to one hour for a single curve, but will undoubtedly be simplified by the development of a mechanical integrator if industrial application brings about sufficient demand for such assistance. The integration has been facilitated by having a supply of

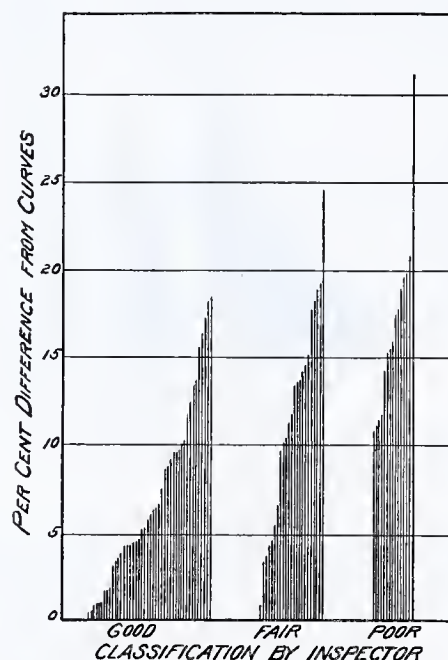


FIGURE 9. GRAPHIC CORRELATION OF COLOR MATCHES WITH DIFFERENCES PRINCIPALLY OF BRIGHTNESS

forms printed in which the series of corrected ordinates may be entered. Figure 8 shows this form in which are entered the data from Figure 7. It should be mentioned here that in any of these calculations the curve recorded by the analyzer must first be corrected, point by point, dividing by the ordinate of the magnesium carbonate curve at that wave length and multiplying by 100.

When two curves for a match in question are each converted into excitation factors by the calculation outlined above, there are obtained three pairs of values, any or all of which may differ. If the two numbers in all three pairs agree closely, the samples must appear alike to the normal eye. In all poor matches the numbers in one or more of these pairs differ markedly. Thus far the largest percentage difference found between corresponding excitation values has been taken as the expression of the difference between two such samples. To illustrate, if the difference in the blue is greater than that in either the green or red, the latter is disregarded and the difference between the samples expressed entirely in terms of the blue excitation values. This is only an approximation, but thus far it has proved satisfactory enough.

Figures 9 and 10 show graphically the correlation in a considerable number of cases in which the judgment of regular inspectors has been compared with the measurements obtained with the color analyzer. They show rather a surprising tolerance on the part of the trade. The allow-

able discrepancy appears greater when the difference is one of brightness than when hue is involved. It must be appreciated that the severity or laxity of the inspector in judging matches is a direct indication of the tolerance allowed by the trade. The consistent use of the color analyzer to assist the inspector in passing doubtful lots would do much to establish a more uniform standard for color matches.

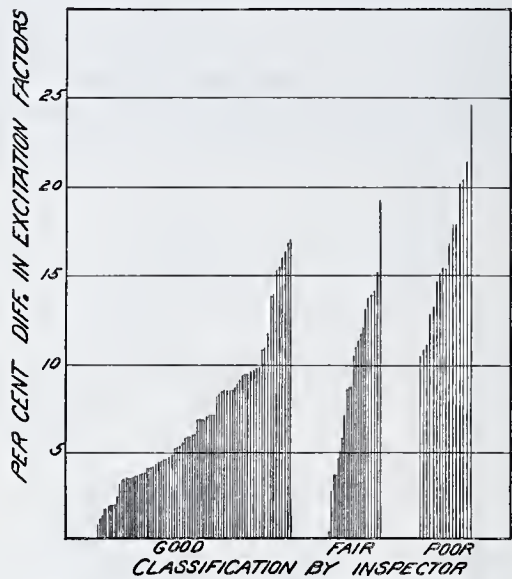


FIGURE 10. GRAPHIC CORRELATION OF COLOR MATCHES WITH PREDOMINATING HUE DIFFERENCES

The use of the color analyzer has proved especially valuable in comparing goods of radically different construction in which individual persons frequently disagree as to whether or not a satisfactory match has been obtained. Attempts have been made to use measurements of dyed yarns to compare with measurements of the color in the fabric obtained from the yarns, but a completely satisfactory method of mounting the yarn sample has not been obtained.

IV. RECORDS OF SAMPLES AFTER FASTNESS TESTS

WASH TESTS. Good washability of fabrics has come to be more and more expected by the customer, and in the case of silks very marked improvement in washability has been shown within the last 5 years. Standard methods of making wash tests have been fairly generally adopted, but the decision as to the degree of loss of color through the washing operation has been left to estimation by eye.

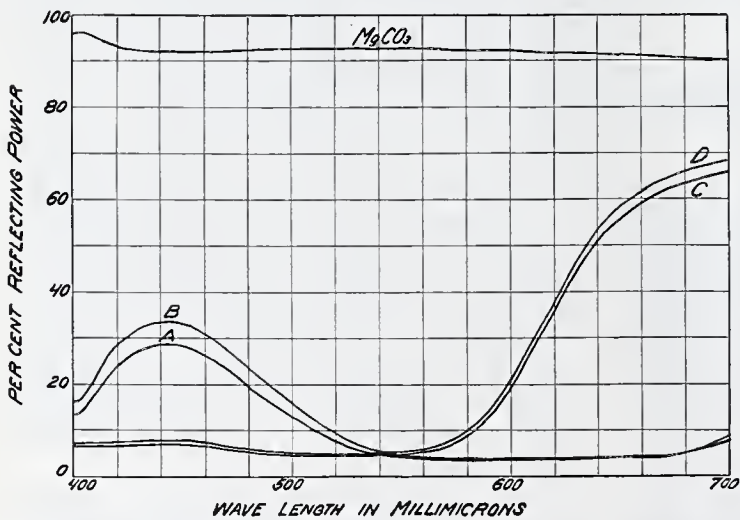


FIGURE 11. CURVES OF SAMPLES BEFORE AND AFTER WASH TESTS

- A. Victoria Blue B before washing
- B. Victoria Blue B after washing, showing unsatisfactory fastness
- C. Erie Scarlet 3B before washing
- D. Erie Scarlet 3B after washing, showing satisfactory fastness

Since the change in appearance of a properly dyed fabric after washing is chiefly one of brightness, it is comparatively simple to apply the color analyzer to obtain a numerical expression for the loss of color during this test. Typical curves from samples before and after wash test are shown in Figure 11. It is only necessary to express the change in terms of per cent difference in reflectance at any one wave length. It should of course be kept in mind that the color analyzer can give only a numerical value to the change that takes place during such a test, and the trade will establish the tolerances based upon commercial practice. However, a tolerance which can be expressed in numerical values is certain to become more uniform and less likely to lead to misunderstanding and disputes.

LIGHTFASTNESS TESTS. Experiments on the fastness of the dyed samples to light were based on exposures to a carbon arc light in the Fade-Ometer. These curves are not so simply interpreted as those for wash tests, since in some cases there is a change in brightness, but more commonly the action of the light causes a distinct change in hue. Typical curves are shown in Figure 12. The same calculation for comparing curves for commercial matches may be applied to curves before and after light exposure.

V. CALCULATION OF FORMULAS FROM CURVES

This section has been included in the outline for a program for application of the color analyzer to textile manufacture, but, because the preceding steps obviously needed to be developed first and because at this time the ability to calculate the dye formula from the curve is of less practical than theoretical interest, there are no data to report here.

In one instance, however, in which goods are dyed by a continuous method (the Cohoe process) ordinary experience in dye application was not adapted to establishing the continuous feed bath required. A study of the substantivity of individual dyestuffs using the color analyzer has proved a solution for this problem and is reported in a paper by W. P. and E. R. Cohoe (1).

SPECIAL APPLICATIONS

For development work in the laboratory where experiments may be carried out under controlled conditions, the color analyzer is invaluable. A simple illustration of a laboratory use has been the establishing of a test for the tarnishing action of velvets intended for the jewelry box trade. The color of a

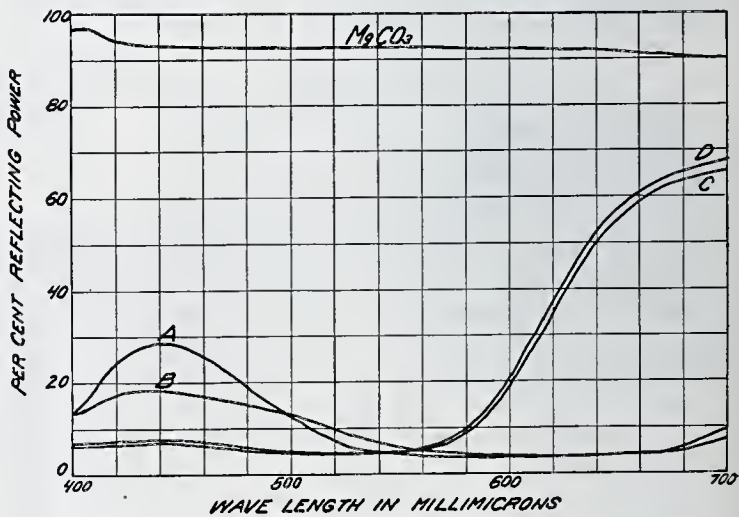


FIGURE 12. CURVES OF SAMPLES BEFORE AND AFTER LIGHT EXPOSURE

- A. Victoria Blue B before exposure
- B. Victoria Blue B after 5 hours in Fade-Ometer, showing objectionable change
- C. Erie Scarlet 3B before exposure
- D. Erie Scarlet 3B after 25 hours in Fade-Ometer, showing good fastness

disk of silver is recorded in the analyzer before and after a standard exposure in contact with the velvet sample, and from the two curves obtained there may be calculated a numerical grading of the tendency of the velvet to tarnish the metal.

CONCLUSION

The work described in this paper is still in progress, but since this program of development may be applicable in other fields and of greater general interest than any detailed and final results, the authors have felt justified in publishing this work at this stage. The expense of the color analyzer and the necessity of an operator with somewhat specialized training will probably limit its use in a plant dyehouse where a simpler form of color comparator is better adapted if and when it is

necessary to supplement the trained eye of the dyer. Special laboratory applications and the use of the analyzer in mill control, particularly in establishing tolerances in commercial matches and for loss of color after wash and light tests, should justify a general recognition of spectrophotometric analysis in the textile industry in the near future.

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Automatic Apparatus for Determination of Small Concentrations of Sulfur Dioxide in Air. III

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EARLIER papers of this series (1, 2) describe the development of a completely automatic apparatus for the determination of traces of sulfur dioxide in air. This apparatus has now been improved and its application extended to the continuous analysis and recording of (1) small concentrations of sulfur dioxide in the field, with a range of 0.01 to about 7.0 p. p. m.; (2) higher concentrations up to about 6 per cent in flue gases which are low in sulfuric acid but contain appreciable amounts of carbon dioxide; and (3) the absorption of sulfur dioxide by plants in laboratory fumigation experiments in the range from less than 0.1 p. p. m. to 50 p. p. m. This paper describes the apparatus for the three purposes mentioned above, and submits confirmatory analytical data on the absorption of the gas by plants.

The machines are built on an angle iron framework and are driven by a small motor operating through the appropriate commercial reduction gears. Steady suction is obtained by means of a small Crowell pump, and the air volume is measured in a wet test meter, which may be provided with an electrical contact on the 1-cubic foot dial, so that the air volume can be recorded on the chart with the sulfur dioxide analysis. Steel cams, 5 inches (12.7 cm.) in diameter, operate the poppet valves as previously described (2). The valves are made from 0.635-cm. (0.25-inch) brass angle valves, as illustrated in Figure 1, and are mounted in solder permanently on a steel plate, care being taken to secure good alignment for the valve rods which are connected with the cam followers through universal joints. The valves have functioned perfectly over a period of more than 2 years. The heavy-wall flexible red rubber bellows will last more than 1 year, and can readily be replaced. The apparatus is connected by block

The application of the acid-hydrogen peroxide method to the continuous analysis of traces of sulfur dioxide in air, as well as higher concentrations in smelter flue gases, is described, and its application to fumigation studies for the absorption of the gas by plants is compared with analyses of the plants themselves for total sulfur, with results which indicate that these analytical machines are capable of a high degree of precision in evaluating the concentration of sulfur dioxide in air.

tin tubing, which is unaffected by the solutions employed. The mercury valves described in the first paper (2) have been replaced by these poppet valves.

Slightly acidulated hydrogen peroxide solution is used as absorbent. In the first and third of the uses for which the apparatus was designed, this solution contains about 0.003 per cent hydrogen peroxide and 0.0005 per cent sulfuric acid.

In the second it contains more peroxide. The increased conductance of the solution, as indicated by a recording Wheatstone bridge, gives a measure of the amount of SO₂ absorbed. A typical assembly is shown in Figure 2, which is a photograph of a laboratory machine. The solution is fed from a large supply bottle, 1, into a constant-level bottle, 2, whence it is measured in a 100-ml. pipet, 3, and placed in an absorber, 4. While the solution in one absorber is being aspirated, the solution in the other is replaced with fresh absorbent. The photograph also shows the motor and reduction gears, 5, the gas meter, 6, the cams, 7, and an assembly of 14 valves, 8.

FIELD MACHINE

The field apparatus is installed in a small well-insulated house, and the gas sample is drawn through a tin tube through the roof, the opening being provided with a screen to exclude insects. The room is provided with a thermograph and in the winter is thermostated.

The field apparatus aspirates each solution for 20 minutes, drawing about 15 liters of air per minute and recording each cubic foot on the chart. This large volume of air causes an appreciable evaporation of the absorbing liquid, with attendant cooling, two factors which tend to compensate each other. The absorbers are mounted snugly in heavy copper

pipes, which reduce the cooling effect so that the latter offsets almost exactly the evaporation of the absorbing liquid. Temperature compensation is obtained with a large volume of

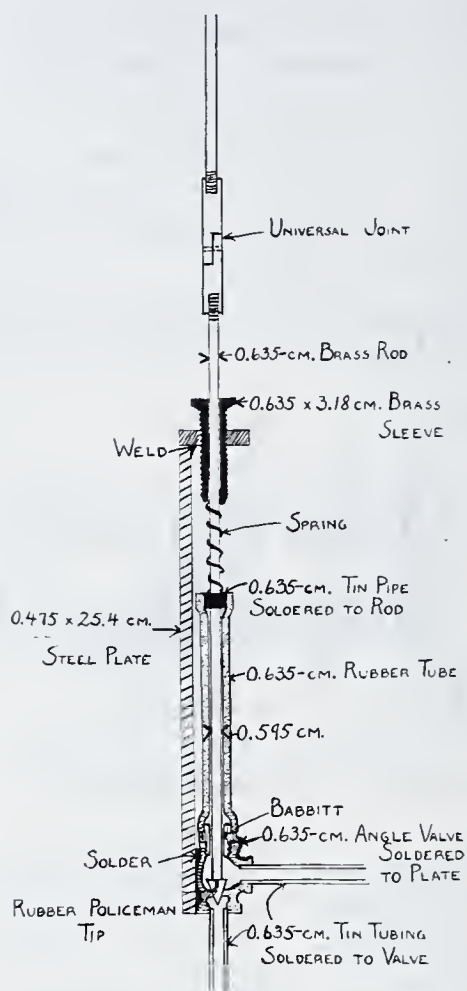


FIGURE 1. SECTION OF MOUNTED POPPET VALVE

approximately 0.002 *N* sulfuric acid in series with the variable temperature rheostat of the recording Wheatstone bridge. By means of a double-pole double-throw switch, this compensating solution can be checked against the regular temperature compensator provided on the recorder. The record shows the concentration over each 20-minute period, but peak concentrations during intervals as small as 1 to 2 minutes can readily be calculated from the slope of the conductance curve.

The apparatus has been used during the past 3 years to determine the sulfur dioxide content of the air near three smelters of the American Smelting and Refining Company, and a number of machines have also been used by investigators of the United States Department of Agriculture and the Canadian National Research Council.

FLUE-GAS MACHINE

It has been demonstrated that the method is applicable to much higher concentrations of sulfur dioxide than occur in the field, and that the presence of carbon dioxide does not interfere appreciably with the determination. An apparatus especially adapted for the analysis of the flue gases has therefore been installed at the El Paso Smelting Works. This machine is provided with two 600-cc. aspirator bottles and a 0.32-cm. copper pipe for drawing the gas sample from the flue. The electrodes in the conductivity cell have a constant of about 2 reciprocal centimeters, so as to permit the measurement of higher concentrations of sulfuric acid. The apparatus operates on a 10-minute schedule, and has been checked against the iodine method of flue-gas analysis.

LABORATORY MACHINE

The laboratory apparatus as finally constructed is particularly well adapted for the study of the absorption of sulfur dioxide by plants in both day and night fumigations, with either high or low concentrations. The absorption is determined by measuring the change of sulfur dioxide concentration of an air stream of known velocity on passing through a fumigation cabinet. The machine operates on a 2-minute schedule. This time period is sufficiently short so that samples from intake and outlet positions in the cabinet may be considered to have been taken virtually simultaneously, unless the concentration in the cabinet is fluctuating rapidly. In very short fumigations, of the order of 15 minutes or less, it is necessary to use two machines in order to get reliable absorption data. For our purpose it is desirable to be able to measure the difference of concentra-

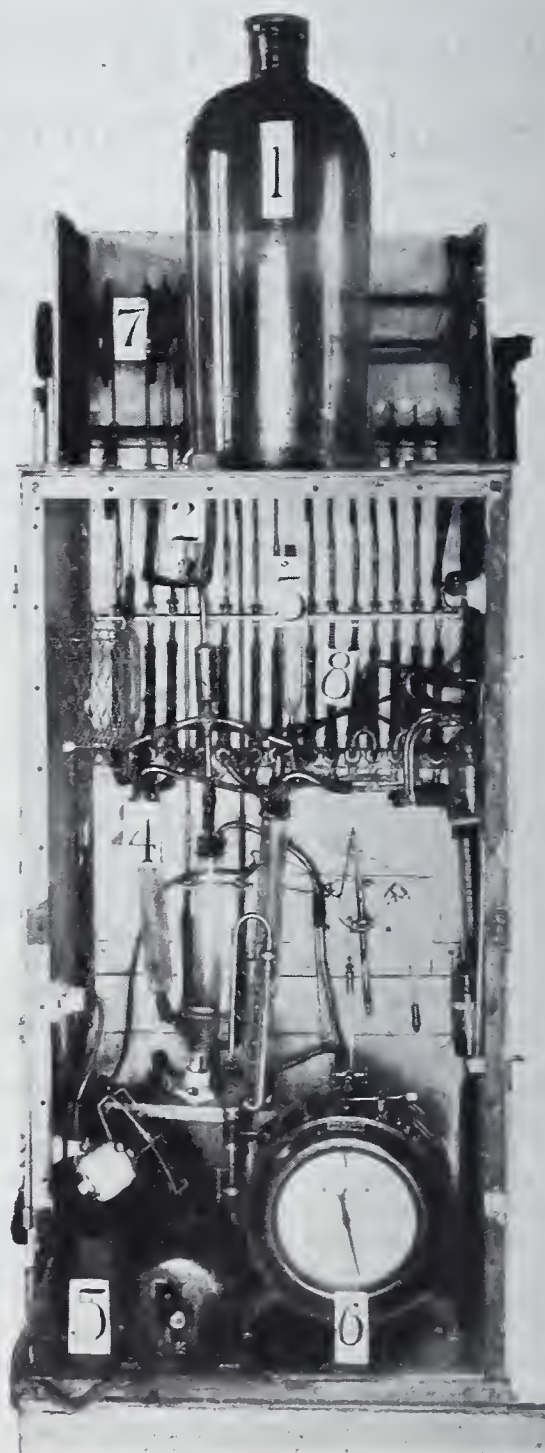


FIGURE 2. LABORATORY PORTABLE SULFUR DIOXIDE AUTOMETER

tion between the intake and outlet positions with an accuracy of at least 1 per cent of the total concentration.

As it is difficult to adjust the two absorbers to register exactly the same concentration under identical conditions of operation, it is necessary to alternate the source of the sample for each absorber so that any machine difference between the two absorbers can be eliminated by averaging the indicated concentrations for each absorber sampling from both intake and outlet. This alternation of the source of the sampling can of course be accomplished by hand in short fumigations, but with long fumigations it is necessary to do it automatically. The laboratory machine (Figure 2) has therefore been provided with a second cam shaft, placed directly underneath, and geared to the first with a reduction of speed of 16 to 1 to operate a system of valves so that each absorber draws one blank sample from the outside air and 7 subsequent samples from either intake or outlet points in the fumigation cabinet before drawing another blank sample, and reversing the source of the sample. The slower moving cam shaft is also provided with four cams, which, when the corresponding cams above are inactivated by raising the nuts on the valve rods, recharge the absorbers only after eight consecutive aspirations, thus permitting the accumulation of the absorbed gas so that concentrations as low as 1 part in 10 million can be measured with a high degree of accuracy.

Although not absolutely necessary to the operation of the machine, the blank aspiration has been found to be useful in calculating the data. The omission of one-eighth of the absorption curve has not often been of any consequence, since the gas concentration is usually uniform.

The whole apparatus is inclosed with light wooden panel and provided with thermostatic control.

ABSORPTION DATA

During the past season a number of fumigations of alfalfa plots have been carried out, using two laboratory machines operating simultaneously and sampling from the same two positions in the fumigation cabinet. The latter is a light metal framework 1.98 by 1.98 by 1.52 meters, covered with sheets of celluloid and mounted in a heavy felt pad on a galvanized iron base. A mixture of sulfur dioxide and air, made uniform by baffle plates in the line, is blown in at the top of the cabinet through a 15.2-cm. pipe and led out through a 20.3-cm. pipe in the base. The sulfur dioxide is supplied from a bottle of the liquid and is controlled by a needle valve and capillary flowmeter. This apparatus is thermostated to yield a steady flow of gas. The air blower can deliver 1400 liters of air per minute, but the volume actually employed is modified by a shutter on the intake, according to the amount of vegetation on the plot.

The concentrations observed in these fumigations are

recorded in Table I, which indicates a very close concordance between the two machines, both as to total concentration and the difference of concentration between intake and outlet positions. In general the concordance in the latter case is better than 1 per cent, the two cases in which this difference is exceeded being in fumigations in which there was an appreciable fluctuation of the concentration in the cabinet.

TABLE I. SULFUR DIOXIDE CONCENTRATION AT INTAKE AND OUTLET OF FUMIGATION CABINET

(Determined by two analytical machines sampling simultaneously from same points)

PLOT	MACHINE	DURATION OF EXPT. Min.	SO ₂ CONCENTRATION		DIFF. %
			Intake P. p. m.	Outlet P. p. m.	
5-14	1	56	6.60	5.70	13.6
	2		6.59	5.58	15.3
5-13	1	58	6.17	5.24	15.1
	2		6.19	5.23	15.5
5-1	1	65	6.17	5.65	8.5
	2		6.21	5.65	9.0
5-2	1	73	6.50	6.10	6.2
	2		6.48	6.05	6.6
4-9	1	70	6.79	6.34	6.6
	2		6.81	6.36	6.6
6-7	1	60	7.02	6.34	9.7
	2		7.00	6.32	9.7
2-7	1	70	5.23	4.60	11.2
	2		5.17	4.59	12.0
3-5	1	125	0.555	0.541	2.5
	2		0.553	0.534	3.3
3-5	1	330	0.276	0.251	10.0
	2		0.270	0.244	9.6
3-5	1	375	0.232	0.213	8.4
	2		0.236	0.216	8.7
3-5	1	120	0.220	0.202	8.2
	2		0.231	0.208	9.9

The volume of air which is sent into the fumigation cabinet is measured by anemometers in both the intake and outlet pipes. The reading of the outlet instrument is usually about 10 per cent lower than the other, and the average of the two readings is taken as the correct volume, on the assumption that about equal portions of gas at both intake and outlet concentrations escaped from the cabinet without going through the outlet pipe. The absorption of sulfur dioxide by the walls of the cabinet is determined by a blank fumigation with the soil completely covered by sheets of celluloid.

The weight of leaves on the plot is found by harvest a few days subsequent to fumigation, allowance being made for additional growth during this period and the percentage of leaves being determined by samples taken at the time of fumigation. The stems are ignored in this calculation, since it has been found that they contain only about 5 to 10 per cent of the added sulfur, even in the case of the two long fumigations in which part of the increase in sulfur in the plants may

TABLE II. ABSORPTION OF SULFUR DIOXIDE BY ALFALFA

(Determined by analysis of SO₂-air mixture and the leaves)

PLOT	DATE 1931	TIME	DURATION OF FUMI- GATION Min.	AIR VOL. L./min.	WT. OF SO ₂ Mg./cc.	CONC. SO ₂ INTAKE P. p. m.	SO ₂ ABSORBED BY:		WT. OF DRY LEAVES Mg.	TOTAL S IN DRY LEAVES		S ABSORBED FROM ANALYSIS OF:	
							Cabinet and plants %	Plants %		Before fumigation %	After fumigation %	Air P. p. m.	Leaves P. p. m.
4-14	8/21	12-1 P. M.	56	8700	2.14	6.60	14.5	13.5	465	310	1.350	1480	1500
5-13	8/25	12-1 P. M.	58	8500	2.14	6.18	15.3	14.3	465	450	1.353	1497	1030
5-1	9/3	3-4 P. M.	65	8250	2.14	6.19	8.8	7.8	278	472	1.310	1.390	590
5-2	9/1	5-6 P. M.	73	8500	2.19	6.49	6.4	5.4	238	604	1.150	1.210	394
4-9	8/28	6-7 P. M.	70	8500	2.23	6.80	6.6	5.6	253	402	1.130	1.210	630
6-7	9/9	11:30 A. M. to 12:30 P. M.	60	8500	2.24	7.01	9.7	8.7	348	310	1.145	1.290	1120
2-7	10/3	12-1 P. M.	70	8500	2.24	5.20	11.6	10.6	368	350	1.265	1.410	1050
3-5	9/22 to 9/25	Continuous	4110	8600		0.384			900	300	1.170	1.450	2900
	9/22 to 10/1		12770	8600		0.320			2400	330	1.170	1.877	7050
3-3	10/8 to 10/27	Continuous	26900	8500		0.202			4920	400	1.200	2.380	12300

have come from the soil. This effect is probably small, however, because samples of leaves taken from a nearby check plot during the fumigation period of plot 3-5 showed no appreciable change of sulfur content.

The absorption values have been checked by analysis of the leaves for total sulfur using the Burgess-Parr sulfur bomb. The leaf samples are taken in large rubber-stoppered test tubes, weighed fresh, then frozen in salt and ice, and allowed to dry in air for about 24 hours before grinding. Analyses are run on 0.7-gram air-dried samples. The procedure is carefully standardized, particularly as to the amounts of reagents and the volume and acidity of the liquid before precipitation with barium chloride. Ten milliliters of 0.1 *N* sulfuric acid are added to each solution as a true blank and the precipitate is allowed to stand 2 to 3 days, with occasional agitation, before filtration.

Table II shows a fairly satisfactory concordance between the sulfur absorbed, as indicated by the analysis of the gas

and the analysis of the leaves. The latter value is in most cases somewhat higher than the former, probably because the absorption took place unevenly on the plants, and there was doubtless a tendency to take as the leaf sample more of the active leaves near the top of the plants, which probably had absorbed more gas than the less active leaves lower down. The uncertainty in the sulfur analysis of the leaves is of the order of several hundred parts per million, owing principally to sampling errors, but also partly to analytical errors. These errors were both minimized by taking at least two samples before and after fumigation and running a number of duplicate analyses on each sample.

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Methods for Microanalysis of Extremely Hygroscopic Substances

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DURING the regular course of analysis, certain series of compounds were found to be so extremely hygroscopic that the existing methods of keeping the material free from water were found to be inadequate. New methods were therefore developed for the analysis of these compounds.

MICRO-DUMAS METHOD

While investigating some extremely hygroscopic derivatives of choline chloride, it was found that a solid micro sample would become liquid in an interval from 10 to 100 seconds. According to the regular method of Pregl (1), the material was weighed in a small weighing tube about 3 mm. in diameter, fitted with a ground-glass stopper. The material, however, became sticky from absorbed water and could not be shaken from the tube properly. The material which was shaken into a shaking bottle became liquid and could not be quantitatively transferred to the combustion tube. The nitrogen values on these compounds ran consistently low and were never within the 0.3 per cent limit of error.

Very good results were obtained, however, by a modification of the Pregl method. A glass-stoppered weighing bottle or "piggie" as described by Pregl, having a diameter of 10 mm. and a length of 40 mm., was cut down to a length of 15 mm. The sample was easily placed in the bottle with great speed. The bottle was then placed in a vacuum desiccator for about 20 minutes. After it had been dried in this way it was stoppered, placed in the balance, and weighed within 5 minutes. Then the stopper was removed and the sample was transferred quickly to the shaking bottle which contained dry powdered copper oxide. The stoppered weighing bottle was weighed at once. The sample in the shaking bottle was mixed with the copper oxide immediately so that the material would not become sticky and adhere to the glass. The vacuum desiccator was situated near the balance so that the weighing tube was kept at the same temperature as the balance. The air which was admitted to the desiccator was passed slowly over magnesium perchlorate trihydrate. Results obtained by this method were quite constant and were only slightly below theory.

ANALYSIS FOR CARBON AND HYDROGEN

Certain compounds of the type $B \cdot 3H_2O$ gave off the exact amount of water ($3H_2O$) as determined by drying experiments on a macro scale. The analysis of B, however, always indicated that the material still held at least 1 H_2O . The material B apparently picked up water very rapidly, as all methods of keeping the sample dry were found to be inadequate. The analyses for carbon in B were seldom within 1 per cent of theory, and the analyses for hydrogen were always high. The material appeared to be very hygroscopic and could not be exposed to the air even for a very few seconds without absorption of moisture. Therefore, the material was dried and analyzed in the following manner: The air-dried material which had been previously analyzed as $B \cdot 3H_2O$ was weighed in a platinum boat and placed in the combustion tube in the same manner as for regular carbon and hydrogen determination. Previously weighed absorption tubes were placed in the usual position to determine the amount of water driven off and to show any decomposition which might take place. Nitrogen was then passed through the tube by way of the regular preheater and drying train at a rate of 5 cc. per minute. The material was heated to 100° to 105° C. by means of a Pregl heating block. The nitrogen was passed over the material for a period of about 90 minutes. The apparatus was then swept out with air for 20 minutes, and the absorption tubes were removed and weighed to determine the results of the drying. When the amount of water was very small it was found necessary to correct for the dehydrite absorption tube which picked up water over the 2-hour period. The weights of the ascarite absorption tubes were very constant, showing little or no decomposition. The absorption tubes were then attached to the combustion tube, and the carbon and hydrogen analysis was carried out in the usual manner. The results were very satisfactory for the material B when entirely free from water.

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RECEIVED January 18, 1932.

Determination of Hydroxyl Number of Oils, Fats, and Waxes

An Accurate, Rapid Method

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THERE is an obvious need for improved technic in the determination of those constituents of the fatty oils and waxes which are reactive with acetic anhydride, inasmuch as the current procedures which serve that purpose are laborious and uneconomical of time and materials and, as applied to rancid materials, inaccurate. The present method of the Association of Official Agricultural Chemists (2) for accomplishing these ends, referred to as the acetyl number, finds its origin in the studies of Benedikt and Ulzer (3) who, proceeding on the theory that the consumption of acetic anhydride is a function of the hydroxyl group to the exclusion of the carboxyl, recommended that the fatty acids of the oil be used as the point of departure. Lewkowitsch, after demonstrating experimentally that anhydrides of the fatty acids are formed in consequence of the dehydrating action of the acetic anhydride when it is used in excess, eventually developed (8) a procedure in which the quantity of acetic acid liberated from the acetylated oil serves as the index of the hydroxyl content of the parent oil. Finally André (1) and then Cook (4), without disturbing the technic of Lewkowitsch but utilizing the stoichiometrical relationships involved in the change in saponification numbers of the oil before and after acetylation, derived a mathematical expression whose application materially simplified the whole operation.

The variable results which are sometimes obtained in the determination of the acetyl number of the same oil by the foregoing procedure are frequently due to the fact that the operator does not arrive at the correct saponification number. For instance, a corn oil showing an initial saponification number of 191.2, after having been subjected to exactly the same washing procedure as for its acetylated product, then possessed a lower value, or 189.7. The percentage error involved in neglecting this situation with reference to oils of low acetyl value, when the latter is calculated with the André-Cook (4) formula, is appreciable. In other instances the presence of soluble, volatile acids, which are lost by washing and drying the acetylated oil, also introduces an error. Hydrolysis of the former in the operation of washing out the excess of acetic anhydride tends towards low results. In fact, this was demonstrated experimentally with a sample of rancid corn oil whose initial acetyl value dropped from 18.93 with five successive washings, each time with 2 liters of hot water and a 15-minute boiling period, to 18.58, 17.01, 16.09, 14.92, and 14.25, respectively. Furthermore, it is not unusual to find a group of operators working in collaboration on the same oils unable to agree among themselves (5, 7) for the same reason, a

The hydroxyl number, defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 gram of fat, oil, or wax, may be determined with economies of sample, reagents, and time if the reaction is carried out in a sealed tube in the presence of acetic anhydride. Upon completion of the acetylation, the excess of acetic anhydride is hydrolyzed and then determined as acetic acid by titration with 0.5 N potassium hydroxide solution. In contradistinction to the current procedure for determining the acetyl number, the entire process is carried out in the presence of the acetylated product except in the case of such samples as contain free soluble acids when filtration, prior to titration, is necessary.

situation which has in the past given rise to the criticism that the chief difficulty of the procedure appears to be in the decomposition and complete removal of the excess of active anhydride (as acetic acid) over that required for the acetylation without causing more or less hydrolysis of the acetylated fat (6). Another criticism of the process is that the fundamental reaction herein involved will not proceed smoothly because excessive amounts of acetic anhydride are made to react with the material under examination for too long a time at the elevated temperatures employed. Undesirable side

reactions, such as aldehyde formation, for example, are thereby made possible.

It appears, then, in the light of the above, that far too many steps are necessary for the determination of this value. The method here offered, serving the same ends as the foregoing one, is simple and accurate, it involves but few operations, and is far from being time-consuming. It is the result of the experiences gained and the information obtained in a critical study of the effect of varying the several major factors which direct the course of most reactions in organic chemistry—time, temperature, and concentration of reactants.

REAGENTS AND APPARATUS

1. Freshly distilled acetic anhydride, 90 per cent purity or better. It should be stored in glass-stoppered amber bottles. Under these conditions it has been found that its keeping qualities are excellent with the result that standardization once a month is sufficient. This operation is carried out in triplicate on 1.5-gram \pm 0.01 samples in the same manner as the determination of the hydroxyl number itself. Its strength should be expressed in terms of milligrams of potassium hydroxide per milligram of reagent. The standardizations should check within 0.0008 mg. of each other.

2. Carbon dioxide-free 0.5 N \pm 0.01 potassium hydroxide solution. It should be adjusted to this strength so that the 50 cc. which are added prior to hydrolysis of the acetic anhydride will be within the proper range.

3. Distilled water. Whenever reference is hereinafter made to water, it should be understood that carbon dioxide-free water is meant.

4. Indicator solutions. Either phenolphthalein or thymol blue may be used, although the latter is preferable.

5. Reaction tubes may be made from 10-mm. soft glass tubing by constricting 300-mm. lengths at the middle and then breaking them at that point. The large end of each tube is then sealed off, thus making two tubes.

PROCEDURE

The sample weight and quantity of acetic anhydride are controlled by the order of magnitude of the probable hydroxyl number as follows:

HYDROXYL NUMBER	ACETIC ANHYDRIDE Grams	SAMPLE Grams
0- 50	1.5 ± 0.01	5.0
50-100	1.5 ± 0.01	2.5
100-200	2.0 ± 0.01	2.5

By means of a calibrated capillary pipet introduce the acetic anhydride into a tared tube, weigh accurately the amount taken, add the sample, and re-weigh. Solids may be added in pellet form. Seal off the tube, place it in an oven at 120° C. for 10 minutes, shake, and then return to the oven leaving it there at rest in a horizontal position for one hour. (Carrying out this reaction under pressure as herein recommended offers no unusual hazards to the operator, for the total pressure within the tube will not exceed 2 atmospheres. Over three hundred acetylations were made during the course of this study without a single accident.)

Open the tube after it has cooled and pour its contents into a 500-cc. Erlenmeyer flask containing 50 cc. of water. Rinse the tube several times, first with cold and then with hot water, finally completing the volume to approximately 200 cc. Now swirl the flask and add exactly 50 cc. of 0.5 *N* potassium hydroxide solution, throw in a few glass beads, attach a reflux condenser, and bring almost to boil over a moderate free flame. (The acetic anhydride is completely hydrolyzed in this operation, the acetic acid being taken up by the water layer.) Rinse down the condenser with 50 cc. of water, wash off the tip of the condenser tube, swirl, cool, and, titrating in the presence of either 10 drops of phenolphthalein or twice as much thymol blue indicator solution, complete the addition of the hydroxide solution.

Solids, such as waxes, which should preferably be heated with the acetic anhydride for 2 hours at 120° C. or 1 hour at 130° C., are best treated as follows: Break the sealed tube in the middle and place it in an Erlenmeyer flask containing 200 cc. of water.¹ Gently warm the mixture until the acetylated wax has melted, swirl, cool, add the 50 cc. of the standard alkali solution, and finally boil the mixture very gently under reflux. Cool and titrate, repeating the process until neutrality is reached. Blanks are run similarly.

Blank determinations are unnecessary in the case of normal samples, but those containing free soluble acids or those highly rancid require filtration prior to titration, the material on the filter paper being thoroughly washed with hot water. In making a blank determination, a weighed amount of the unacetylated oil is thoroughly washed with hot water on a moistened filter paper and the washings titrated.

CALCULATION

Convert all buret readings to their equivalents in terms of milligrams of potassium hydroxide. To find the quantity of the latter involved in this reaction, subtract that required to neutralize the excess of acetic anhydride (as acetic acid) from that equivalent to the amount of the former taken for acetylation of the sample. Then the hydroxyl number, which is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 gram of fat, oil, or wax, is calculated as follows:

$$\frac{\text{mg. KOH involved}}{\text{weight of sample}} = H$$

If desired, the acetyl number also may be calculated from these data by means of the following formula:

$$\frac{\text{hydroxyl number}}{1 + 0.00075 H} = \text{acetyl number}$$

The value 0.00075 represents the stoichiometrical relationships involved in the increase in molecular weight of the material under examination because of the exchange of the hydrogen atom of the hydroxyl group for an acetyl radical.

In the development of this method for determining the hydroxyl content of fatty oils and waxes, many data were obtained in the search for a suitable method for hydrolyzing the excess of acetic anhydride and its quantitative estimation as acetic acid. Space does not permit of a detailed discussion, nor does one seem to be particularly necessary. Of peculiar interest, however, are the data pertinent to the time-temperature-concentration factors in the acetylation of the material under examination. Typical data, illustrative of the manner in which these variables affect, respectively, the hydroxyl number of oils of high and low acetyl values, are presented in Table I.

TABLE I. EFFECT OF VARIATIONS IN TIME, TEMPERATURE, AND CONCENTRATION UPON HYDROXYL NUMBER

OIL	APPROX. CONCENTRATION OF REACTANTS		TEMPERA- TURE ° C.	TIME Hours	HYDROXYL NUMBER
	Oil Parts	Acetic anhydride Parts			
Castor	1.0	1.0	100	1	129.5
	1.0	1.0	100	2	149.2
	1.0	1.0	100	4	163.9
	1.0	1.0	100	6	164.5
	1.0	1.0	100	10	164.4
	1.0	1.0	110	1	162.2
	1.0	1.0	110	2	164.8
	1.0	1.0	110	4	164.4
	1.0	1.0	110	10	164.7
	1.0	1.0	120	1	164.5
	1.0	1.0	120	2	164.3
	1.0	1.0	120	4	164.9
	1.0	1.0	120	6	164.2
	1.0	1.0	120	10	164.7
	1.0	1.0	130	10	164.3
	1.0	1.0	140	10	164.6
	1.0	1.0	150	10	164.0
	1.0	1.0	120	1	164.3
	2.5	2.0	120	1	164.5
	2.5	1.5	120	1	163.3
	2.5	0.9	140	2	163.6
Olive	1.0	1.0	100	1	4.7
	1.0	1.0	100	2	4.9
	1.0	1.0	120	1	4.9
	1.0	1.0	120	2	5.3
	1.0	1.0	120	6	4.5
	1.0	1.0	140	3	5.0
	2.5	1.0	140	2	5.0
	5.0	0.2	140	2	4.2
	5.5	1.5	120	1	5.0
	5.0	1.0	120	1	4.8
	5.0	0.7	120	1	4.6

In the interaction of acetic anhydride and castor oil, for all practical purposes here typifying ricinolein, is seen an example of the statement that reaction rates are doubled for every 10-degree rise in temperature, since the same stage in the equilibrium of this reaction, as indicated by the hydroxyl number, was reached in 4 hours at 100° C., in 2 hours at 110° C., and in 1 hour at 120° C. In much the same way this condition obtained in the case of olive oil. It was from the information gained by the mode of procedure suggested by the data recorded in Table I that the optimum ratios of sample weights to acetic anhydride, and time and temperature considerations, were selected.

The stability of the acetylated product when prepared as herein described from normal, nonrancid material is seen—taking castor oil as an example—in the fact that the reaction product can be boiled without fading of the end point after neutralization of the excess acetic anhydride (as acetic acid). On the other hand, the acetylated product from a rancid oil—the corn oil cited in the introductory paragraphs serves as an example—will behave in quite a different manner. In this case, acid will be liberated every time the solution is boiled following a period of rest. The quantity of acid set free on

¹ An alternative procedure is to use purified chloroform in removing the acetylated product, in which case, however, the solvent must be removed before the final titration. The possibility of losing acetic acid in this operation must not be overlooked.

hydrolysis of the reaction products will gradually diminish. The source of this hydrolysis is evidently not traceable to acetyl derivative of hydroxy acids, for the behavior of the castor oil belies such an assumption, nor is it brought about by the breaking down of mixed anhydrides. Rather it appears to be due to the presence of either unstable acetylated mono- and diglycerides, or some acetylated oxidation products of the fatty acids. The observed instability of an acetylated mono-*n*-valerin under the above conditions (it was found that the acetyl number of the parent compound cannot be determined at all by the official method (2) and only approximately by the proposed one) supports the former view.

A very important step in the determination of the acetyl number under the present mode of procedure (2) is that excessive washing of the reaction mixture be avoided. In fact, Lewkowitsch (9) cautioned against more than three applications of wash water. Yet, even when this precaution is observed, it is necessary to use at least 1.5 liters of wash water. No such situation arises, however, in carrying out this determination under the proposed procedure, for when conditions are such as to make a blank determination desirable (see description of method), the volume of water necessary to hydrolyze the anhydrides of the soluble fatty acids which have been formed is small; in fact it is not enough to cause a measurable hydrolysis of the major acetylated product. The presence of insoluble (higher) fatty acids does not introduce an error, for the action of acetic anhydride upon them is such as to form their corresponding anhydrides (9). These are very stable, even on continued boiling. Since equivalent quantities of acetic acid are formed in this reaction, none of its anhydride is actually consumed, a condition which would make a blank determination unnecessary in this case.

By way of comparison of the two methods for determining acetyl numbers, there is included in this report a set of typical data (Table II). It will be observed that there is a satisfactory agreement in results when the necessary correction for

interfering substances has been applied. Hydroxyl and acetyl numbers are practically the same in the bracket below twenty.

TABLE II. COMPARISON OF OFFICIAL AND PROPOSED METHODS FOR DETERMINATION OF ACETYL NUMBER

MATERIALS	ACETYL NUMBER		HYDROXYL NUMBER
	Official method	Proposed method	
Oils:			
Olive	5.0	4.9	4.9
Cottonseed	5.9	5.5	5.5
Sesame	3.3	3.8	3.8
Tobacco seed (extracted)	9.0	8.6	8.7
Tobacco seed (expressed)	4.8	5.3	5.3
Peanut	5.4	5.1	5.1
Rye germ	20.2 ^a	21.0 ^a	21.5 ^a
Corn	16.7 ^b	17.7	17.9 ^c
	15.4 ^b	18.1	18.3 ^d
Castor	146.3	146.4	164.5
Waxes:			
Beeswax	24.2 ^e	26.3	26.8
Carnauba	44.7	44.7	46.2

^a Analyses by Albert W. Stout.

^b Values calculated from saponification number of washed original sample. They will be several points lower if carried out by official method.

^c Filtered before titration, correction for blank was applied.

^d Titrated in presence of acetylated product. No blank applied.

^e Some constituents apparently lost along with coloring matter which dissolved in acetic anhydride during the process of acetylation. Original product was bright yellow, final a pure white.

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Determination of Small Amounts of Methyl Chloride in Air

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IN CONDUCTING an investigation of the toxicity of small amounts of methyl chloride in air, it was necessary to check the computed concentrations by chemical analyses. Of the various methods (1, 4, 5, 6) reported in the literature, none of them appeared suitable for the purpose at hand. Attempts were made, therefore, to develop a method which would be satisfactory for the conditions outlined, and thus a procedure which proved satisfactory was devised.

Allison (1) determined methyl chloride by absorption in glacial acetic acid and also by burning with an excess of oxygen in an Orsat gas apparatus. McKee (4) and Nicloux (5) also used a combustion method similar to that of Allison. Roka and Fuchs (6) heated methyl chloride with methanol and sodium iodide in a pressure flask to form methyl iodide, which they distilled into silver nitrate. It is obvious that none of these methods would be suitable for small amounts of methyl chloride in air—as, for example, 50 p. p. m. by volume (3).

BUREAU OF MINES METHOD

The procedure adopted is very similar to the Referees method for determining total sulfur in fuel gases. The air

containing the methyl chloride is mixed with natural gas and burned in a microburner. The halogen products formed combine with ammonia obtained from ammonium carbonate cubes placed around the burner, and also with ammonium hydroxide formed by the ammonia from the ammonium carbonate and the water in the products of combustion of the gas. The chlorides produced are collected and determined by the Vohlard method.

APPARATUS. Figure 1 shows the apparatus. The methyl chloride-air mixture is added as the primary air supply to burner *a*, shown in detail in Figure 2 and described later. Secondary air enters around the base of the burner. The products of combustion of the fuel gas, the methyl chloride and excess secondary air, are carried by convection up through the trumpet tube *b* and are impregnated with ammonia which emanates from the ammonium carbonate cubes piled around the burner (Figure 2). In the presence of the water vapor some of the halogen reacts with the ammonia and is deposited on the walls of the upper part of the trumpet tube. The remainder enters a glass marble-filled absorption tower, *c*, where the surfaces are wet with ammonium hydroxide formed by the condensation of water vapor in the presence of am-

monia. This absorbs additional halogen products of combustion. The excess condensate drips from the tower into a beaker. The effluent vapor from the tower is led through a Cottrell precipitator which collects any halogen-bearing smoke or fog that escapes the tower. The precipitator is made by sealing a platinum wire concentrically in a glass tube, *d*, which has a side outlet at each end. The outside of the tube is wrapped with tin or copper foil to within about 4 inches of each end, and the foil is bound in place with friction tape. A wire wound around the foil with one end protruding through the tape serves as one terminal and the platinum wire as the other, both being connected to the secondary of a Ford spark coil, *e*. The current for the spark coil is obtained from a 110-volt 60-cycle lighting circuit through a toy transformer, *f*, adjusted to give 6 volts. It is obvious that other designs of electrical precipitators may be used, providing they readily permit a washing out of the precipitate.

Figure 2 is a detailed sketch of the burner. It is constructed by placing a glass T tube tightly over the burner stem of an ordinary laboratory microburner, *g*, and sealing the primary air intake with wax, *h*. A piece of platinum gauze, *i*, is fused onto the burner tip to stabilize the flame. The connection between the stem and the arm of the T tube is made gas-tight by means of a rubber tubing collar. The fuel gas enters at *j* and the methyl chloride-laden air at *k*. Secondary air enters between the trumpet tube wall *l* (shown in entirety in Figure 1) and a cork base, *m*, which supports ammonium

carbonate cubes, *n*. The cork is covered with a sheet of asbestos, *o*. This cork is smaller than the base of the trumpet tube in order to permit secondary air to be drawn by convection or the stack-effect of the trumpet tube and tower above.

The above burner design, and in fact much of the other equipment described, was an assembly of parts readily available in the laboratory. Other designs and parts which will carry out the prin-

ciple of the method will be satisfactory. This also applies to the fuel, which may be any combustible gas not containing an appreciable amount of halogen compounds. A blank determination using the fuel employed must, of course, be made.

EXPERIMENTS MADE TO TEST METHOD

The accuracy of the method was tested by making a series of determinations of carefully measured amounts of methyl

A method for the determination of small amounts of methyl chloride in air is described. The apparatus and procedure are in many respects similar to the Referees method for total sulfur in fuel gases. Tests of the method using amounts of methyl chloride ranging from 12.36 to 30.74 mg. have shown the error to be less than 2 per cent of the amount present for the lower, and less than 1 per cent for the upper limits of the range used. In developing the method, a range of concentrations from 200 to 1600 p. p. m. or 0.02 to 0.16 per cent by volume was used. The method has also been used for the determination of dichlorodifluoromethane vapor in air, and is suggested for the determination of other organic halide gases and vapors.



the microburet was measured at atmospheric pressure and the prevailing temperature, after which it was corrected to 0° C. and 760 mm. Hg. A minimum of stopcock grease was used.

CHEMICALS AND REAGENTS USED. The methyl chloride used was obtained from the Roessler and Hasslacher Chemical Co., and according to specifications was 99.5 per cent pure. The silver nitrate solution used was approximately 0.025 *N* and was standardized against standard hydrochloric acid. The hydrochloric acid was standardized using sodium carbonate prepared by heating sodium bicarbonate. The potassium sulfocyanate was standardized against the silver nitrate. Ferric alum was used as an indicator. Calibrated burets were used in making all titrations.

DILUTION AND BURNING OF SAMPLE. The methyl chloride which was confined in the microburet was forced into a stream of air by opening the stopcock at the top of the buret and slowly displacing with mercury. The air was measured and the rate controlled by means of a dry meter, and the mixture led through glass tubing to the microburner previously described. All connections were glass-to-glass held in place by rubber tubing. The volume of the samples varied from approximately 5.5 to 13.5 cc. of methyl chloride. The air was admitted through the meter at the rate of about 20 liters per hour. The time of burning for the 13.5-cc. samples was approximately 1 hour, for the 10-cc. samples from 20 minutes to 1 hour and 20 minutes, and for the 5.5-cc. samples from 45 minutes to 1 hour and 30 minutes. This gave a range of concentrations varying from about 200 to 1600 p. p. m. by volume, or 0.020 to 0.16 per cent. Blank determinations were made on room air and gave an average titration of 0.05 cc. of silver nitrate, the equivalent of which was 0.07 mg. of methyl chloride. This blank titration was subtracted from the silver nitrate values in the determinations.

DETERMINATION OF CHLORIDES. The chlorides were washed from the trumpet tube, Cottrell precipitator, and absorption tower until the washings gave a negative test for chlorides. It was found that this was best accomplished in the tower by quickly pouring 4 or 5, 50-cc. portions of water over the beads. This procedure prevented channeling and produced a solid column of water which resulted in more efficient scrubbing. The washings were added to the condensate which collected and dropped from the tower during the combustion, and the chlorides were then determined by the Volhard method. The silver chloride was removed by filtration through a Gooch crucible prior to the sulfocyanate titration.

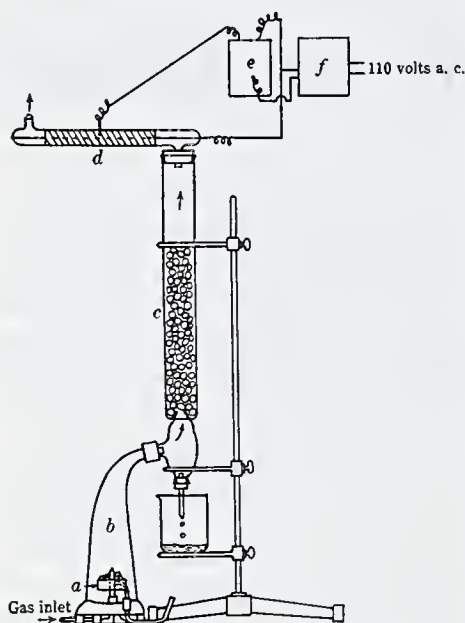


FIGURE 1. APPARATUS FOR DETERMINING METHYL CHLORIDE IN AIR

TABLE I. DETERMINATIONS WITH KNOWN AMOUNTS OF METHYL CHLORIDE

VOL. OF CH ₃ Cl (99.5% AT 0° C. 760 MM.) TAKEN Cc.	CH ₃ Cl Mg.	VOL. OF AIR Liters	AVER- AGE CONCN. P. p. m.	AgNO ₃ TITRA- TION Cc.	CH ₃ Cl RECOV- ERED Mg.	RECOV- ERY %	ERROR %
13.43	30.12	22.5	600	21.14	30.00	99.6	-0.4
13.71	30.74	22.5	610	21.87	31.03	100.9	+0.9
13.67	30.68	19.0	710	21.53	30.56	99.7	-0.3
13.51	30.32	20.0	670	21.37	30.32	100.0	0.0
9.95	22.32	7.0	1250	15.85	22.47	100.6	+0.6
10.07	22.60	6.3	1600	16.00	22.68	100.3	+0.3
10.07	22.60	24.7	410	15.85	22.47	99.4	-0.6
10.02	22.48	10.7	940	15.79	22.39	99.6	-0.4
5.60	12.57	13.5	370	9.02	12.70	101.5	+1.5
5.60	12.57	19.0	290	8.81	12.46	99.2	-0.8
5.58	12.52	17.2	330	8.79	12.43	99.4	-0.6
5.52	12.38	27.5	200	8.87	12.54	101.3	+1.3
5.51	12.36	19.0	290	8.79	12.43	100.5	+0.5

RESULTS. The results of the determination, given in Table I, show that the accuracy of the method with amounts of methyl chloride ranging from about 20 to 30 mg. is in the neighborhood of 0.5 per cent, being at least within 1 per cent in all cases. When amounts as low as 12 mg. are determined, the accuracy is nearer 1 per cent, being better than 2 per cent in all cases.

The equivalent of 0.1 cc. of the silver nitrate solution used was 0.14 mg. of methyl chloride. A titration error of 0.1 cc. would cause an error of approximately 1 per cent in samples weighing about 12 mg. Therefore, the per cent error of the method depends primarily on the weight of methyl chloride in the sample taken rather than on the concentration. This fact should be borne in mind in any attempt to extend further the range or accuracy of this method.

PROCEDURE USED FOR ROOM ATMOSPHERES CONTAINING METHYL CHLORIDE. The above method has been used in this laboratory to check concentrations of methyl chloride ranging from 50 to 600 p. p. m. by volume in air which were used for toxicity experiments with animals. The atmosphere to be analyzed was taken from the animal exposure chamber with a small rotary air pump and delivered through a dry meter to the burner. A by-pass between the blower and the meter permitted the excess air from the blower to return to the chamber. The rate of burning and size of flame depended upon the concentration of methyl chloride in the air, a slower rate and smaller flame being used for higher concentrations. The above procedure gave results which were within 5 per cent of the values computed from flowmeter measurements of the volume of methyl chloride and air used in the mixture that entered the gas chamber. The results were always lower than the computed values and, aside from flowmeter errors and control, may be partially explained by the fact that the Cottrell precipitator was not used in this particular set-up of apparatus.

TABLE II. ABSORPTION OF METHYL CHLORIDE (from a 1 per cent methyl chloride-air mixture) BY CONTACT WITH DISTILLED WATER IN GAS-ANALYSIS PIPET

NO. OF PASSES INTO PIPET	ABSORPTION OF CH ₃ Cl, ACCUMULATIVE			BLANK, USING ROOM AIR ACCUMULATIVE ABSORPTION
	Sample 1 %	Sample 2 %	Sample 3 %	
1	5	5	a	0.04
2	a	a	5	a
5	15	a	6.5	0.03
10	26.5	20	19.5	-0.01
20	45	40	35.0	-0.01
30	50	46	45	a
40	55	57.5	a	a
50	a	65	62.5	a
60	a	75	66.5	a
70	a	75	71.5	a
80	a	75	72.5	a
90	a	a	72.5	a
100	a	a	72.5	a

a Not determined.

The sampling procedure, as described, may be modified in accordance with other common procedures for sampling gases. For example, it is obvious that samples of atmospheres

may be taken by air displacement in containers of suitable size and delivered to the apparatus by sweeping into the burner with a stream of air; or if the samples are relatively small they may be delivered to the apparatus by mercury displacement. Owing to solubility of methyl chloride in water, the use of water as a displacing medium should be avoided, though if absolutely necessary, it may be used if care is taken to avoid operations that facilitate solution of the gas in the liquid. If the water is not agitated a great deal or left in contact with the gas-laden air, it is possible to use it without vitiation of the results for practical health investigations. Experiments were made in which methyl chloride-air mixtures were passed from a mercury-filled buret into distilled water contained in a Haldane type gas-absorption pipet at room temperatures (2). Table II gives the results of these experiments.

The practical use of water as a displacing liquid was also studied. Three determinations were made using 19-liter samples of 600 p. p. m. methyl chloride-air mixture obtained in and delivered from a 20-liter aspirating bottle by use of distilled water as the displaced and displacing medium. The results obtained were 98, 95, and 96 per cent, respectively, of the calcu-

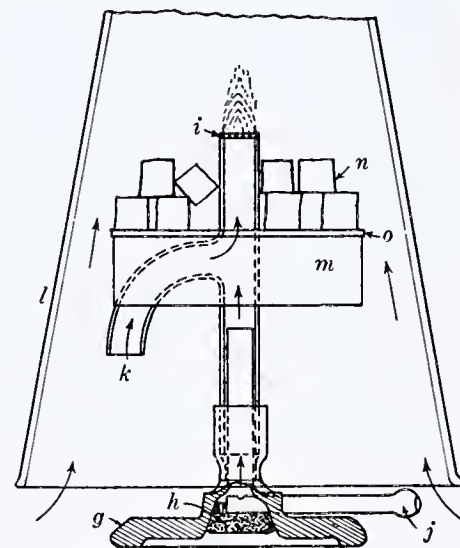


FIGURE 2. DETAIL OF BURNER

lated amount of methyl chloride in the air. The surface of the water was disturbed very little, but no special precautions were used to prevent motion other than removing and admitting water under the water surface.

The line to the burner was flushed by drawing a few liters of room air into the aspirating bottle and then forcing this air to the burner.

In judging the size of samples, the allowable per cent error and the probable error of method must be considered.

USE OF METHOD FOR OTHER ORGANIC HALIDE GASES AND VAPORS

The same apparatus has been used to determine dichlorofluoromethane, and dichlorodifluoromethane in concentrations of 2 and 20 per cent, respectively. In dealing with these relatively high concentrations, the samples were taken over mercury and diluted with air prior to combustion. The results agreed well with other methods of analysis, and point to the applicability of this method to the determination of other organic halide gases and vapors in air.

ACKNOWLEDGMENT

The development of the method described in this report was a necessary part of an investigation of the response of animals to methyl chloride in air which was conducted coöperatively by the Roessler and Hasslach Chemical Company and the Bureau of Mines. The development was carried out at the Pittsburgh Experiment Station of the Bureau of Mines under the direction of its chief surgeon, R. R. Sayers.

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Some Titer Points of Mixed Fatty Acids

II. Mixtures of Pure Fatty Acids

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THE titer points of fatty acids and of mixtures of fatty acids is of such importance commercially, both in evaluating fats and in using them, that a better understanding of their behavior is desirable. Continuing the work reported previously (3), the titer points of mixtures of relatively pure fatty acids were determined. It was expected that these figures would furnish indications, at least, of the causes underlying the seemingly erratic results obtained in several cases with commercial fats and oils. This was found to be true, but the behavior observed needs elucidation and consequently no explanation can be attempted until further data have been secured. The particular fatty acids predominating in the fats or oils to be mixed apparently determined the character of the resulting titer curve. The several other fatty acids usually present, although in much smaller amounts,

influence the curve somewhat, but to just how great an extent has not yet been determined.

The four fatty acids selected for this work were lauric, myristic, palmitic, and oleic. The selection was determined principally by the fact that mixtures of the glycerides of these (together with that of stearic acid) in varying proportions form the majority of the commonly occurring nondrying oils and fats. The other acids, such as caproic, caprylic, capric, linoleic, etc., are present in much smaller quantity.

The lauric, myristic, and palmitic acids were the specially purified grade of the Eastman Kodak Company. The oleic acid was purified in the laboratory, using a high-grade commercial red oil as the source, by the lead salt-ether method with subsequent fractionation under reduced pressure.

That none of these acids was strictly chemically pure is recognized. It is a very difficult matter to effect the absolute separation of the fatty acids from one another (2), especially when acids close to each other in the series are under consideration, and for the present purpose strict chemical purity is not essential. The acids used were, however, of a relatively high degree of purity.

The titer point is not a value of as high an order of accuracy as are some of the other physical constants. It varies within certain limits according to the method employed in determining it, the exact technic exerting considerable influence upon the result. The amount of fatty acid used, the method of stirring, the differential in temperature of fatty acid and surrounding bath, and the number of times the titer has been read on the same portion of fatty acid are a few only of the variables which must be standardized because no particular method can be considered the only correct one. Because of this factor of inherent variability in the titer itself, absolute purity of the fatty acids was not considered essential.

PROCEDURE

The fatty acids were kept dry and, just before determining the titer point, were weighed out carefully in the desired proportions in a 50-cc. glass beaker; they were heated to about 115° C., thoroughly mixed, and, after cooling somewhat, were transferred to the titer tube. Determination of the titer from this point on was in accordance with the method of the Fat Analysis Committee of the AMERICAN CHEMICAL SOCIETY (1).

The results are reported in the form of curves which are plotted with the titer points as ordinates and the percentage composition of the mixed fatty acids as abscissas.

DISCUSSION OF RESULTS

As it was desired to learn in the first place the effect of mixing two acids adjacent to each other in the same homologous series (considering only acids with an even number of carbon atoms), lauric and myristic were selected. The curve resulting

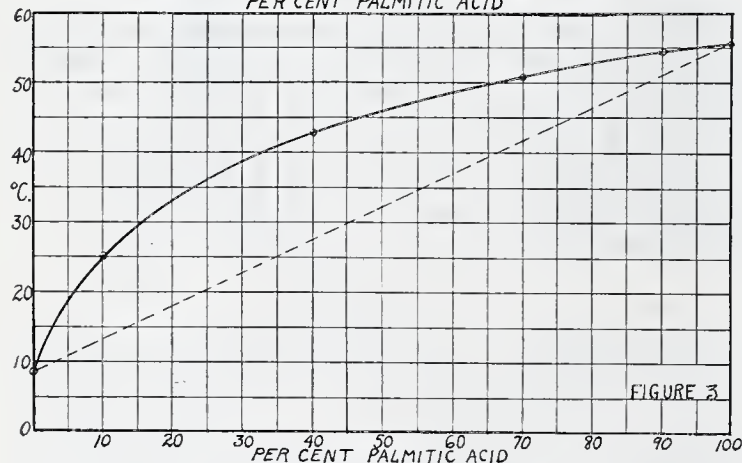
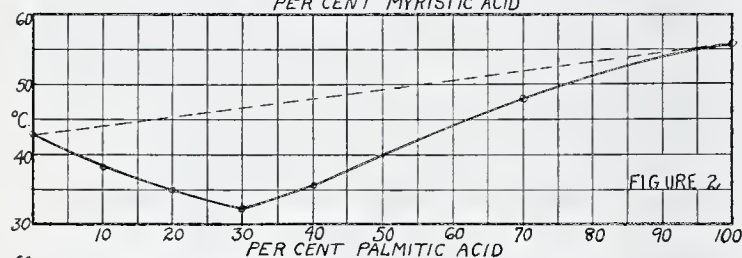
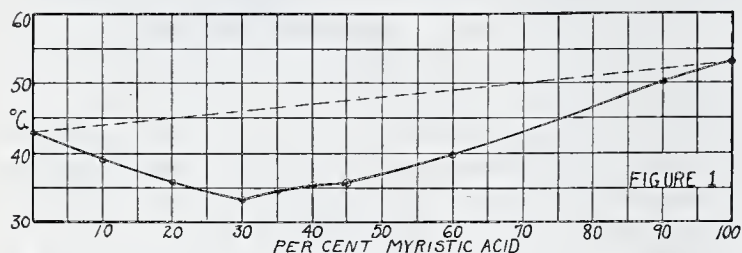


FIGURE 1. TITER CURVE FOR MIXTURES OF LAURIC AND MYRISTIC ACIDS

FIGURE 2. TITER CURVE FOR MIXTURES OF LAURIC AND PALMITIC ACIDS

FIGURE 3. TITER CURVE FOR MIXTURES OF OLEIC AND PALMITIC ACIDS

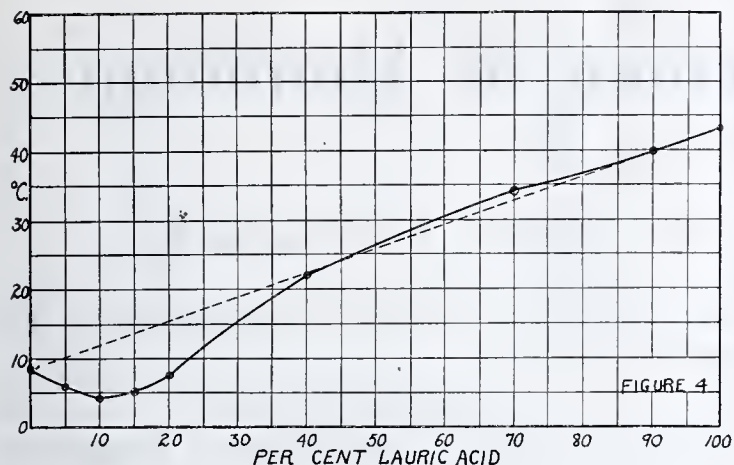


FIGURE 4

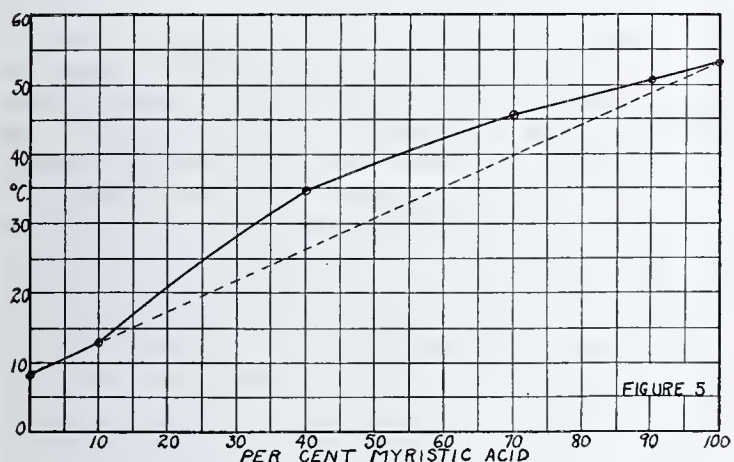


FIGURE 5

FIGURE 4. TITER CURVE FOR MIXTURES OF OLEIC AND LAURIC ACIDS

FIGURE 5. TITER CURVE FOR MIXTURES OF OLEIC AND MYRISTIC ACIDS

(Figure 1) shows the depressing effect upon the titer of the addition of a higher titered material. This is similar to the effect upon the melting point observed in general when two materials similar chemically are mixed, but in the case of fatty acids no generalization can be made. The lowest point was reached with the mixture containing 30 per cent myristic acid.

Mixtures of lauric and palmitic acids (Figure 2) give a curve similar to Figure 1, but distinguished by the fact that palmitic acid, although having a higher titer, exerts a greater depressing effect upon the titer than does myristic acid. The low point, however, is reached at the mixture containing 30 per cent palmitic acid, just as 30 per cent myristic acid gave the low point in Figure 1. At approximately 60 per cent lauric acid the two curves cross each other and from there on the mixtures containing palmitic acid have the higher titer. At the point of greatest depression the titer of the mixture of lauric and palmitic acids is almost 15° C. below the "mean line." This is the line connecting the titers calculated arithmetically from the titers of the two pure acids involved (3).

Mixtures of saturated acids with an unsaturated acid were tried next. Because its glyceride is a constituent of so many different naturally occurring oils and fats, oleic acid was selected as the unsaturated acid. Figure 3 shows that the addition of a high titered acid (palmitic) raises the titer of the mixture even from the beginning, contrary to the effect observed in the two previous cases. The rise is abrupt and remarkable, reaching in one portion of the curve a point 16° C. above the mean line.

Figure 4 shows the effect of mixing lauric acid with oleic. Instead of raising the titer of the mixtures, as did palmitic acid, it depresses it sharply at the beginning, and not until

44 per cent is present does the titer reach that on the mean line. At no place is the curve much above this line.

As might be expected in view of the two preceding results, the addition of myristic acid (intermediate in position in the series between lauric and palmitic) to oleic, as shown in Figure 5, gives a curve intermediate in form between that for lauric and palmitic acids. The titers of all mixtures are either on the line or above it, but there is no abrupt or great rise in any portion.

That it is not possible to generalize about the behavior of the titer of mixtures of other acids until further data have been secured is apparent in view of the results obtained with these four acids. Mixtures of several other saturated acids, both with a less and with a greater number of carbon atoms, must be tried, and these acids in turn mixed with oleic. Another unsaturated acid—linoleic—present in corn oil, cottonseed oil, etc., as well as in the drying oils such as linseed, must be used before any attempt can be made to explain or predict the behavior of mixtures of naturally occurring oils and fats.

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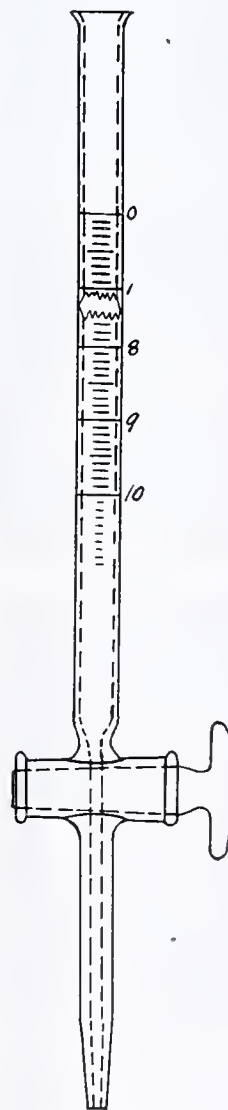
New Specification for Burets

WITHROW MORSE, Röhm and Haas Co., Bristol, Pa.

BY MEANS of a few marks representing tenths of cubic centimeters below the lowest graduation of a buret, many exasperating errors of passing this mark can be obviated. Few chemists have escaped these experiences, owing to diverted attention, defective eyesight, poor light, or other cause. The added graduations should be shorter than the standard marks to insure against mistaking them for divisions of the lowest cubic centimeter of the buret.

Frequently the buret is used as a large pipet of the Mohr type. In such a case the additional marks serve a useful function where a few tenths of a cubic centimeter are demanded beyond the decimal aliquot (10 cc., 50 cc., 100 cc.). Refilling the buret to accommodate a fraction of a cubic centimeter is obviated.

The Arthur H. Thomas Company kindly prepared a buret to this specification.



MARKED BURET

RECEIVED March 2, 1932.

Determination of Sodium in Aluminum

I. Chemical Analysis

R. W. BRIDGES AND M. F. LEE, Aluminum Research Laboratories, New Kensington, Pa.

THE problem of determining sodium in aluminum is not a new one. As early as 1859, Sainte-Claire Deville (24) developed a leaching method for the determination of sodium. He converted the aluminum to nitrate, ignited at low temperature, and leached the alkalis with water. This method has been used or modified by Diehl (8), Richards (23), Hunt, Langley, and Hall (14), Moissan (18), Jean (15), Seligman and Willott (26), Kohn-Abrest (16), Belasio (3), Bhattacharyya (5), Pattison (22), Villavecchia (27), and Bertiaux (4). Handy (13) dissolved aluminum in hydrochloric acid and nitric acid, ignited gently, and applied the J. Lawrence Smith method to the oxides formed. Allen (1) dissolved aluminum in hydrochloric acid, made an ammonium hydroxide separation, and determined alkalis in the filtrate. Nicolardot (19) proposed to disintegrate the aluminum with mercuric chloride, filter, and determine alkalis in the filtrate. When small amounts of sodium and large amounts of aluminum are present, these methods do not achieve quantitative recovery of the sodium.

An electrolytic method has been proposed by Gaith (12) in which the aluminum is dissolved in hydrochloric acid, the excess acid neutralized with calcium carbonate, the copper group removed as sulfides, and the resulting solution electrolyzed with a mercury cathode and carbon anode. The amalgam is decomposed with sodium chloride and the sodium hydroxide formed is titrated. This method has been tried by several workers without success. Aluminum hydroxide is formed during the electrolysis, and doubtless occludes much sodium.

The uranyl acetate method is considered the best gravimetric procedure. Difficulty in securing satisfactory magnesium acetate has led to unsatisfactory results with the magnesium uranyl acetate method of Caley and Sickman (7). However, the zinc uranyl acetate method of Barber and Kolthoff (2) gives satisfactory results. Feldstein and Ward (10) used nickel uranyl acetate. Of the longer and more tedious methods, those of Fairlie and Brook (9), and of Schürman and Schöb (25) are feasible. The limitation of these methods is that the sodium content of aluminum is for the most part 0.01 per cent or less, which makes a gravimetric determination very difficult.

From a qualitative test used in the Aluminum Research Laboratories, a quantitative procedure called the fusion-leach method has been developed. This method takes advantage of the fact that when aluminum is held just above the melting point the sodium comes to the surface of the metal and forms sodium compounds which, after cooling, may be leached out with water. The alkalinity so produced is titrated and the fusion and leaching repeated until the sodium is removed. The method cannot be applied to aluminum containing other alkali or alkaline earth metals. Fortunately, these are absent as a rule or present in negligible amounts. Results obtained with the fusion-leach method have been checked satisfactorily with the uranyl acetate and nitrate crystallization methods. One good feature of the fusion-leach method is that besides being the shortest chemical method, it is applicable over the range of 0.001 to 0.05 per cent sodium, in which the sodium content of aluminum and aluminum alloys is usually found. The uranyl acetate method is not applicable for determination

of sodium below 0.01 per cent. Procedures for these three methods follow.

FUSION-LEACH METHOD

SPECIAL REAGENTS. One-hundredth *N* sulfuric acid; 0.01 *N* sodium hydroxide.

PROCEDURE. Place approximately 50 grams of metal (if sodium is between 0.001 and 0.01 per cent) or 25 grams (if sodium is between 0.01 and 0.05 per cent) in an iron crucible fitted with a water-cooled lid. Place the crucible in a crucible furnace fitted with a transite cover cut so that only two-thirds of the crucible is directly exposed to the heat. Apply sufficient heat to melt the metal and then just enough to hold it in a molten condition for 15 minutes. Cool the button and transfer to a 250-cc. beaker. Wash the crucible and cover into the beaker containing the button. Add enough water to cover the button and allow to stand for 15 minutes. Remove the button, rinse, add two drops of methyl red, and titrate with 0.01 *N* sulfuric acid, using approximately 0.5 cc. in excess. Boil for 5 minutes and titrate back with 0.01 *N* sodium hydroxide, and repeat the fusion and leaching until the net titration falls to 0.5 cc. or less. The number of leachings necessary will depend on the sodium content.

$$\text{Per cent sodium} = \frac{\text{net titration in terms of 0.01 } N \text{ sulfuric acid} \times 0.023}{\text{weight of sample}}$$

URANYL ACETATE METHOD

SPECIAL REAGENTS

SOLUTION A		SOLUTION B	
	Grams		Grams
Uranyl acetate	10	Zinc acetate	30
Acetic acid	6	Acetic acid	3
Water to make	65	Water to make	65

Mix solution A with solution B and allow to stand for at least 24 hours. Filter before using.

PROCEDURE. Dissolve 1 gram of sample in a minimum amount of 1 to 1 hydrochloric acid, filter, and evaporate to a volume of 5 cc. Add 100 cc. of zinc uranyl acetate solution, stir for 45 minutes with a mechanical stirrer, and allow to stand overnight. Filter through a Gooch or sintered-glass crucible. Wash first with reagent, then twice with ethyl alcohol and six times with acetone. Dry for 30 minutes at 105° C. and weigh as sodium zinc uranyl acetate. A blank must be carried through in parallel with the determination.

$$\text{Sodium} = \text{sodium zinc uranyl acetate} \times 0.01495$$

NOTE. Instead of weighing the sodium zinc uranyl acetate precipitate, its sodium content may be calculated from a volumetric determination of the uranium by the following procedure: Dissolve the washed precipitate with hot water, add 15 cc. of 1 to 1 sulfuric acid, and weak potassium permanganate until pink. Add a few zinc shot, warm gently for 15 minutes, cool, filter through a cotton plug into a beaker containing 100 cc. of cold water, and titrate with potassium permanganate of suitable strength (0.07 *N* and 0.02 *N* have been used). A blank must be carried through with the determinations.

A comparative study of the gravimetric method and the volumetric method has been made and the results obtained are given in the following table:

SODIUM WEIGHED AS $\text{NaZn}(\text{UO}_2)_2\text{Ac}_2 \cdot 6\text{H}_2\text{O}$
%
0.44
0.45
0.29
0.30
0.15
0.15
0.074
0.074
0.037
0.037
0.015
0.008
0.0016

SODIUM DETD. VOLUMETRICALLY BY TITRATION OF URANIUM
%
0.44
0.45
0.29
0.30
0.14
0.14
0.074
0.074
0.037
0.036
0.014
0.008
0.0017

Blenkinsop (6) has proposed a method in which the uranium is determined by reduction with titanium chloride. McCance and Shipp (17) have introduced a colorimetric method in which the uranium is determined with potassium ferrocyanide.

NITRATE CRYSTALLIZATION METHOD

SPECIAL REAGENTS. Mercuric chloride, saturated solution. Special nitric acid. Eight parts of 70 per cent nitric acid to 7 parts of water.

PROCEDURE. Weigh on a rough balance an 8-inch (20.32-cm.) quartz dish, add 250 cc. of water, 10 cc. of mercuric chloride solution, 30 grams of fine aluminum drillings, and warm gently until reaction starts. Add 10 cc. of concentrated nitric acid and heat until vigorous reaction starts. Place the dish in a cooling pan and slowly add 390 cc. of concentrated nitric acid. If the mass becomes viscous, add another 100 cc. of water. When apparent action has ceased, heat on a hot plate until the solution of the sample is complete. If the weight of the liquid falls below 600 grams before solution is complete, add special nitric acid. Finally evaporate the solution to 600 grams, cool, with continual stirring, in a water bath, and, when dish and contents are cold, allow to stand for 1 hour or more. Filter the crystals formed through a 5-inch (12.7-cm.) Büchner porcelain funnel, using suction to dry the crystals. Press well with a flattened rod, and, when dry, wash with 50 cc. of concentrated nitric acid. Allow the wash acid to stand on the crystals for a few minutes before suction is again applied. Receive the filtrate in a 4.5-inch (11.43-cm.) quartz dish. Evaporate the solution until a hot saturated solution is obtained, crystallize, and allow to stand as before. Filter through a quartz funnel,

receiving the filtrate in a 3.25-inch (8.25-cm.) quartz dish. Wash with 10 cc. of concentrated nitric acid, add 2 cc. of concentrated sulfuric acid, evaporate to dryness and bake until no more fumes are evolved, cool, add 10 cc. of ammonium hydroxide, and allow to stand overnight. Warm, filter into a platinum dish, return the paper to the dish, add 5 cc. of concentrated hydrochloric acid, macerate the paper, warm, and precipitate with ammonium hydroxide. Filter, and wash with hot, slightly ammoniacal 2 per cent ammonium chloride solution. Combine the filtrates and evaporate to approximately 25 cc., add 10 drops of concentrated sulfuric acid, pass in hydrogen sulfide gas, filter, and evaporate the filtrate to dryness. Ignite to drive off ammonium salts, add a few cubic centimeters of water and 2 cc. of saturated ammonium carbonate solution, filter, evaporate to dryness, and ignite for 30 minutes at 500° C., cool, and weigh. Add a few drops of water, 2 drops of ammonium hydroxide, warm, filter, ignite the paper at 500° C., cool, and weigh. The loss in weight is sodium sulfate. The filtrate should be examined for magnesium.

Return the crystals from the first and second crystallizations to the 8-inch (20.32-cm.) quartz dish, add 150 cc. of concentrated nitric acid and 50 cc. of water, evaporate to 580 grams, cool, and recrystallize. Repeat the procedure outlined above. Deduct a determined reagent blank.

$$\text{Sodium} = \text{sodium sulfate} \times 0.3238$$

Some results obtained by the foregoing methods are as follows:

SAMPLE	FUSION-LEACH METHOD	NITRATE CRYSTALLIZATION	URANYL ACETATE
	%	%	%
1	0.040	0.040	
2	0.016	0.015	
3	0.009	0.010	
4	0.008	0.009	
5	0.040		0.038
6	0.017		0.016

ACKNOWLEDGMENT

The authors wish to acknowledge the contributions made by W. I. Sivitz, formerly of Aluminum Research Laboratories, and P. M. Budge, chief chemist of the Fairfield Works Laboratory, toward the development of the fusion-leach method.

♦ ♦ ♦ ♦

II. Spectrographic Analysis

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THE determination of sodium in aluminum may be made by means of the spectrograph, and the results agree with chemical analysis within satisfactory tolerances. Chief among the advantages of the spectrographic determination, as contrasted with chemical determinations, is the rapidity with which a series of results can be reported. Eight to ten specimens may be examined within 2.5 hours, or an average of not more than 20 minutes per sample. The presence of other alkalis or alkaline earths does not interfere with the determination and, at the same time, the presence or absence of such impurities is established.

Methods using both the direct current arc and the condensed spark have been investigated. Solution of the metal in acids with subsequent arc excitation of the dry salt, as used by Nitchie (20) in the analysis of zinc, was not entirely successful because of the relatively low solubility of aluminum and the strong continuous spectrum of the graphite electrodes in the region of the sensitive sodium lines. The sodium con-

tent of the solvents is also to be considered. Sparking the metal did not seem sensitive enough to warrant an attempt at development, as the smallest amounts could not be detected and the intensity gradient was not well marked for the higher amounts.

The method which seems most applicable for determining sodium in aluminum is arc excitation of the metal itself between electrodes of graphite. Papish and O'Leary (21) determine chromium in fused alumina by the arc. Fesefeldt (11) uses a similar method for determining beryllium in aluminum oxide. Metallic aluminum cannot be used very successfully as electrodes with the arc because of its relatively low melting point and the formation of a heavy crust of oxide on the tips which is nonconducting and nonvolatile. However, the metal burns readily in the graphite arc and, when used in this way, the continuous spectrum of the graphite is practically eliminated.

Since solutions have not been found successful for this

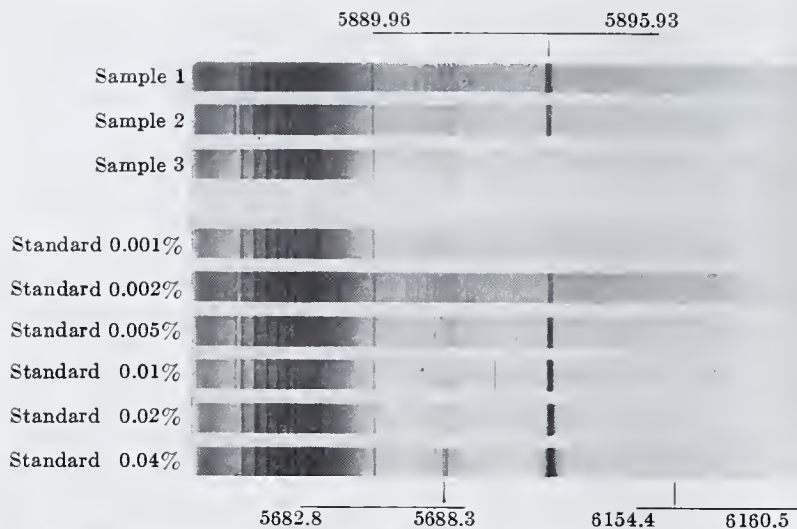


FIGURE 1. DETERMINATION OF SODIUM IN ALUMINUM BY FIRST METHOD

Sample 1, 0.008%; sample 2, 0.005%; sample 3, 0.0015%

determination, synthetic standards are necessarily eliminated. Therefore, the standards used are samples of aluminum which have been carefully analyzed by the available chemical methods. A series of these standardized metals containing 0.000, 0.001, 0.002, 0.005, 0.01, 0.02, and 0.04 per cent sodium have been prepared and are used for all spectrographic determinations.

Sodium in aluminum is estimated by four of its lines, the *D* lines at $\lambda\lambda$ 5889.97 and 5895.93, and the green lines at $\lambda\lambda$ 5682.68 and 5688.22. The *D* lines serve for amounts up to 0.02 per cent. The green lines are just visible at 0.02 per cent and are more valuable for estimating amounts between 0.02 and 0.04 per cent, as they show a gradation of intensity which is more apparent to the eye than that of the *D* lines (Figure 1). The sensitive ultra-violet doublet at λ 3303, al-

though more sensitive than the green pair, is in general not so valuable, as aluminum sometimes contains a small amount of zinc, and in such cases the sodium lines are rendered useless by the zinc lines at λ 3303. For this reason, no attempt has been made in these laboratories to utilize the ultra-violet sodium lines. A Littrow auto-collimating spectrograph with a quartz optical system is used for the determination. Eastman process panchromatic plates are used for photographing the spectra.

PROCEDURE. Two 1.25-inch (3.18-cm.) lengths of 0.25-inch (0.64-cm.) diameter round Acheson graphite rods are used for the electrodes. (A separate set is necessary for each sample photographed.) Drill a $\frac{7}{32}$ -inch (0.56-cm.) hole in one end of one of the pieces about 0.25 inch (0.64 cm.) deep. This piece serves as the lower and positive electrode and supports the metal. The upper electrode is used solid. Place the two pieces of graphite in the steel holders of the arc stand and give them

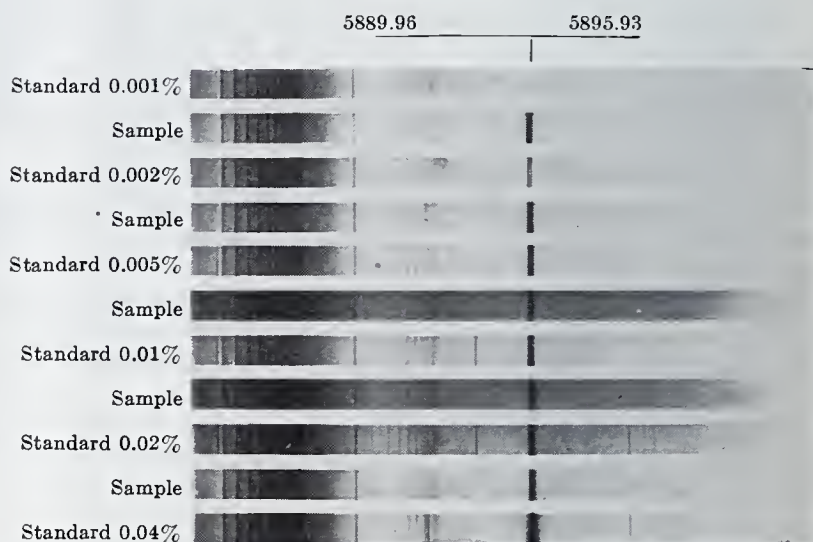


FIGURE 2. DETERMINATION OF SODIUM IN ALUMINUM BY SECOND METHOD

Sample alternated with standards; sodium estimated as 0.01%

a preliminary burn for about a minute with a current of 6 amperes. This step is to volatilize any sodium in the electrode tips or any which may have been placed there by handling. Saw or shear from the specimen a section about $\frac{3}{16}$ inch (0.48 cm.) square by $\frac{3}{8}$ inch (0.95 cm.) long. Place this piece of metal in a small beaker or crucible and cover with strong nitric acid. Place on a hot plate and heat near boiling for 4 or 5 minutes. Remove the metal from the acid with forceps, wash with distilled water, and dry. Place in the cavity of the lower electrode. With the spectrograph in correct adjustment, strike the arc and give an exposure of 1.5 minutes, with a current of 6 amperes at about 50 volts. The voltage is maintained as nearly constant as possible by focusing the images of the tip of the upper electrode and the image of the sample on two horizontal lines ruled on the slit diaphragm. This procedure keeps a constant distance between the two electrodes which is about all that is necessary to insure constant voltage. The samples for analysis and the standard samples are exposed under conditions as nearly identical as is possible.

Comparison with standards is accomplished in either of two ways, one possessing the advantage of requiring less time, the other that of being somewhat more accurate. The two methods are illustrated in Figures 1 and 2, respectively. In both schemes, intensities are matched visually without the aid of a measuring device such as a densitometer. The first

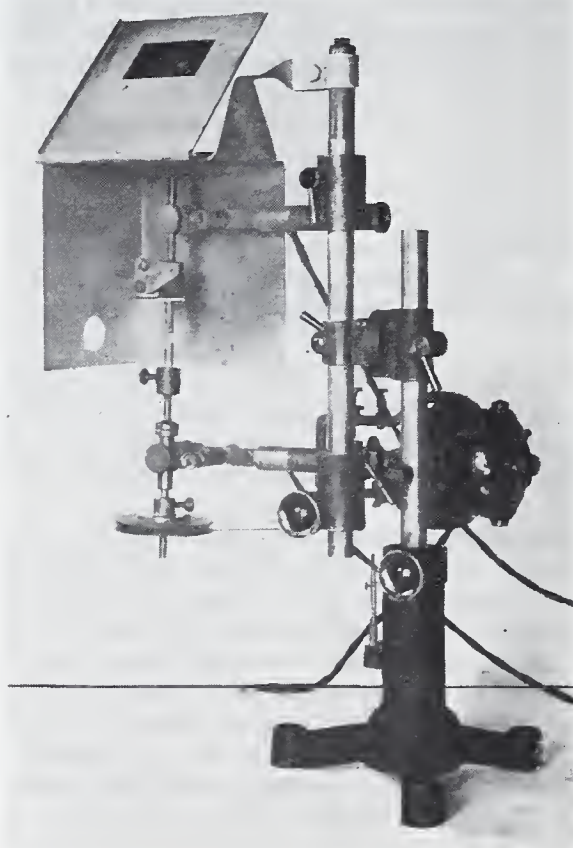


FIGURE 3. ARC STAND WITH ROTATING ELECTRODE HOLDER AND MOTOR

method consists of photographing all the samples, in duplicate if desired, on one portion of the plate, and then adding all the standards on another portion of the plate, as in Figure 1. The second method alternates each sample with the standards so that the spectrum of the sample is always between two standards. Obviously, a better opportunity is offered for matching intensities, as shown in Figure 2. Small differences in sodium produce such noticeable differences in intensity that the second method is rarely used, the first being considered accurate enough for ordinary requirements.

This method of analysis is based on the assumption of a constant exposure with an excess of metal always in the arc. To assist in accomplishing this end, a rotating holder for the lower electrode and a timing device are used. The rotating electrode holder shown in Figure 3 is made of steel with a fiber pulley, and is driven by a small motor mounted on the arc stand. Rotating the metal during the exposure keeps the image of the flame centered on the slit. Without this feature, the flame has a tendency to wander around the edges of the specimen or the graphite, often being shifted laterally enough to be thrown off the slit entirely. Accurate timing is controlled by means of a specially built device actuated by a Telechron motor. The apparatus is wired as an auxiliary circuit through a system of relays which allows the Telechron motor to run only when the arc is burning. As soon as the predetermined interval is complete, the timer opens the main contractor in the arc circuit and extinguishes the arc. A similar appliance is mentioned by Nitchie (20). Control of the exposure by some such means is very desirable when accurate timing is essential, as in this determination. The arc may be extinguished several times in a single exposure because of an oxide film, a draft of air, or other reasons. With such a device to record the successive intervals as they occur, the total exposure will be the same in time, regardless of the number of interruptions.

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Mineral Composition of Dates

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THE chemical composition of the date is of interest because of the widespread use of this fruit as a human food. In the date-producing countries of the Orient and northern Africa it is a principal component of the diet. France and Italy import many dates from their colonies across the Mediterranean. In England the annual consumption is 3 pounds per capita, whereas in Canada and the United States it is respectively 1 pound and 0.43 pound. The date industry in California and Arizona is important and is growing rapidly, the present production being over 3,000,000 pounds per year. The American-grown dates, however, furnish only a small fraction of those consumed, for approximately 54,000,000 pounds of dates are imported annually, principally from Iraq.

Although there are many varieties of dates, only a few are of commercial importance. The Deglet Noor is the principal American-grown variety, while the Hallowi, Sayer, and Khadrawi comprise the greater part of the annual import. The present paper is concerned particularly with the more important imported varieties, Hallowi and Sayer.

PROXIMATE COMPOSITION

Numerous proximate analyses of dates have been reported in the literature. However, to show the general composition

of dates, proximate analyses of packaged samples of Hallowi and Sayer varieties purchased on the market were made and are presented in Table I. These samples were grown in Iraq and were packed by the Hills Brothers Company of New York.

TABLE I. PROXIMATE COMPOSITION OF EDIBLE PORTION OF IRAQ DATES

	HALLOWI %	SAYER %
Moisture	19.0	18.0
Ash	2.22	1.59
Protein (N \times 6.25)	1.72	2.16
Fat (ether extract)	1.90	0.31
Reducing sugars as invert	73.50	...
Total carbohydrates other than crude fiber	73.67	76.14
Crude fiber	2.17	1.90
Sucrose	None	...

The moisture content of bulk dates varies from 12 to 21 per cent, about 17 to 20 per cent being that of a palatable date. It may become considerably less in storage. As the date dries out, the dextrose crystallizes. Sugared dates are considered inferior both by the trade and by the public, but they can be restored to a suitable moisture content by treatment with moist steam. Dates with a moisture content below 23 per cent will keep satisfactorily, because the high sugar concentration inhibits the growth of microorganisms.

The high percentage of sugar, approximately 75 per cent, gives the high calorific value of 1420 calories per pound (3). In this respect dates are practically on a par with figs and raisins, but higher than prunes.

The percentage of protein is low, approximately 2 per cent. In the date-producing countries of the Orient and northern Africa the natives unknowingly compensate for this in their diet of dates and milk.

Sucrose, as the table indicates, is lacking in the Hallowi date. Slade (4) was the first to note that there are two types of dates: the invert type, possessing at maturity a large amount of invert sugar and little or no sucrose; and the cane sugar type, possessing at maturity practically all of its sugar in the form of sucrose. The imported varieties, Hallowi and Sayer, are of the invert type, while the principal American-grown variety, the Deglet Noor, is of the cane sugar type.

The percentage of ash is high and is comparable to that of other dried fruits.

The ratio of edible portion to pit is variable in different varieties of dates, but at a definite moisture content is relatively constant for a given variety. Thus at 18 per cent moisture the Hallowi yielded on an average 89.6 per cent of flesh and 10.4 of pit; Sayer yielded 91.2 and 8.8 per cent.

MINERAL COMPOSITION

The amount and composition of the ash are shown in Table II. Methods of analysis of the Association of Official Agricultural Chemists (2) were used in obtaining the data presented in this table, with the exception of the data for iron and copper. Iron was determined by means of the thiocyanate method as modified by Stugart (5), and copper by the method of Ansbacher and his associates (1), using xanthate colorimetry. Each of the values given is the average of results from the analysis of two samples, one representative of a 72-pound case of Iraq dates from the 1929 crop, the other representative of a similar case from the 1930 crop.

The percentage of ash, approximately 2 per cent, is two or three times as high as that of most of our foods which yield an alkaline ash. Most fresh fruits and many vegetables have less than 1 per cent of ash. Other dried fruits, such as prunes and raisins, have a percentage of ash comparable to that of dates, but it must be pointed out that, in their manner of use

in the diet, dates are more in the class of fresh fruits than in that of dried fruits.

The outstanding characteristic of the ash is the large proportion of potash. Calcium, in which the greatest deficiency in the mineral nutrients of common food occurs, is also present in considerable amount. Phosphorus, likewise sometimes deficient in common foods, is present to the extent of 7 to 10 per cent of P_2O_5 .

TABLE II. MINERAL COMPOSITION OF EDIBLE PORTION OF DATES

	HALLOWI %	SAYER %
Total ash, moisture-free basis	2.02	1.94
Alkalinity of ash ^a	16.7	15.9
Composition of ash:		
K ₂ O	42.7	40.8
Na ₂ O	2.47	2.65
CaO	4.51	6.96
MgO	5.86	6.77
P ₂ O ₅	9.50	7.47
Fe ₂ O ₃	0.26	0.23
Al ₂ O ₃	0.48	...
CuO	0.015	0.014
Cl	13.33	16.64
SO ₃	6.44	7.62
MnO	0.21	0.30
SiO ₂	7.01	7.24

^a Cc. of *N* HCl required to neutralize the ash from 100 grams of moisture-free edible portion.

The alkalinity of the ash is high because of the large proportion of potash. Ash from 100 grams of edible portion is equivalent to from 13.6 to 14.7 cc. of normal alkali. The following data, taken from Sherman (3), give a basis for comparison: spinach, 27.0; raisins, 23.7; dried beans, 18.0; lettuce, 7.4; potatoes, 7; tomatoes, 5.6; oranges 5.6; lemons, 5.5; apples, 3.7.

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RECEIVED September 9, 1931. Presented before the Division of Agricultural and Food Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931. Part of the thesis presented by M. M. Cleveland, Hills Brothers Research Fellow, in partial fulfillment of the degree of Master of Science.

Rapid Centrifugal Method for Pectic Acid Determination

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IN THE course of extended studies on the heat extraction of fruit juices for jelly manufacture (5), the writers gaged the efficiency of extraction by a determination of the pectin (or pectic acid) in both juices and marc. After comparing various chemical precipitation or titration methods, including those of Carré and Haynes (3), Ahmann and Hooker (1), and Wichtmann (2), the latter was found to be the most direct and yielded reasonably satisfactory results. Briefly the method consists of a double precipitation of pectic substances with ethyl alcohol, filtration, and subjecting the aqueous pectin solution to a mild alkaline hydrolysis under controlled conditions to form pectic acid. The latter is then precipitated by addition of hydrochloric acid, filtered, and washed free from the acid and finally dried, weighed, ignited, and reweighed. The technic is extremely time-consuming and

only moderately accurate. Pectin itself is difficult to estimate. The only reasonably satisfactory procedure is precipitation with alcohol as tentatively recommended by the A. O. A. C. (2). Pectic acid may be roughly computed to pectin or vice versa, though various fruits have different ratios. In the Baldwin apple, the pectic acid-pectin is approximately 1.0 to 1.7, and for liquid apple pectin, 1.0 to 2.0. Pectin itself is not a simple substance, but is rather a complex of several closely allied carbohydrate derivatives having galacturonic acid as an essential constituent (7, 9). However, alcohol precipitation yields not only pectins, but gums, proteins, etc., which are insoluble in alcohol. Notwithstanding these facts, this crude technic is the basis of nearly all quantitative work on the pectic substances of plants.

Experiments were conducted on a centrifugal method for determining pectin (alcohol precipitate). Using 15-ml. tapered, graduated centrifuge tubes, much time was spent in attempting to throw down alcohol precipitate in an even, compact layer that could be measured. All efforts were unsuccessful. The pectin formed bulky gelatinous precipitates of varying physical properties and densities and could not be centrifuged with success.

After much preliminary work, the method for pectic acid as here described was worked out.

RAPID PROXIMATE METHOD FOR PECTIC ACID

Depending on the concentration, measure at room temperature 5 or 10 ml. of fruit juice free from sediment, or other filtered pectinous solution, into a 15-ml. tapered, graduated glass centrifuge tube. If 5 ml. of juice are taken, dilute to the 10-ml. mark with water. Add 1 ml. of 10 per cent sodium hydroxide, mix, and let stand for 15 minutes. The alkali hydrolyzes the pectin to pectic acid. Then add 2 ml. of 10 per cent hydrochloric acid solution to precipitate the pectic acid and mix thoroughly. Place the tubes (usually twelve at a time) in a wire basket immersed in a water bath near the boiling point, and allow to flocculate for 8 to 15 minutes, or until flocculation is complete. Stir with a small glass rod to remove air bubbles and to prevent floating, and thus hasten the formation of the uniform, flaky precipitate. Cool to below 25° C., centrifuge at 2400 to 2500 r. p. m. for 15 minutes on a 14-inch head, and immediately read the volume of precipitate. Make the reading by turning the tube upside down at eye level.

If fruit or pulp is used, prepare the sample by boiling 100 grams with 200 ml. of water for 1 hour, replacing at intervals the water lost by evaporation. After transferring to a 500-ml. volumetric flask and cooling, adjust the volume to exactly 500 ml. and filter through filter paper. Aliquots of this solution may be used for samples. If too dilute, the solution may be concentrated to a definite volume by evaporation.

STANDARDIZATION OF TECHNIC

Such variables as quantities of sample, alkali and acid, speed of pectin hydrolysis, speed and optimum temperature of flocculation and centrifuging were studied experimentally.

Enough sample should be taken so that from 0.7 to 1.5 ml. of centrifuged precipitate are obtained. When more pectic acid than this was present, difficulty was experienced during the precipitation with hydrochloric acid and subsequent flocculation because of the bulk of the precipitate. Very small amounts of precipitates always gave high results and did not pack down well during centrifuging. Between 20° and 25° C. no temperature effects were observed.

Fruit juices are sufficiently similar in acidity that the hydrolysis of the pectin is carried out at a fairly definite hydroxide-ion concentration. An excess of alkali broke down the pectin too quickly and gave a dark brown liquid from which the hydrochloric acid incompletely precipitated the pectic acid and left it in poor physical condition. The time required for hydrolysis as shown by quantitative determination of pectic acid was variable for the several pectin solutions

A new, simple, rapid, proximate method for the determination of total pectic substances as pectic acid in fruit juices, extracts, or pectin solutions is described. The filtered sample, in a 15-ml. tapered, graduated centrifuge tube, is hydrolyzed under controlled conditions by alkali, and the resulting pectic acid gel is precipitated by hydrochloric acid, flocculated in a water bath, cooled, and centrifuged. The volume of precipitate is correlated with results obtained by the usual long gravimetric method.

The method is particularly adapted to the routine examination of a large number of samples of pectin solutions of similar composition. In a series of fifty-five trials with six products, the per cent deviation ranged from 2.9 to 12.6. The results are accurate to about 5.5 per cent.



cold unflocculated gel was centrifuged. At times excellent checks were obtained, but the results were too variable to be of great value. Since a larger volume of precipitate is secured by not flocculating the gel, more accurate readings should follow. After many trials it was decided that the more uniform readings of the centrifuged flocculated precipitate were preferable to the greater volume of the centrifuged gel. It may be possible to manipulate this pectic acid gel so that it can be satisfactorily centrifuged.

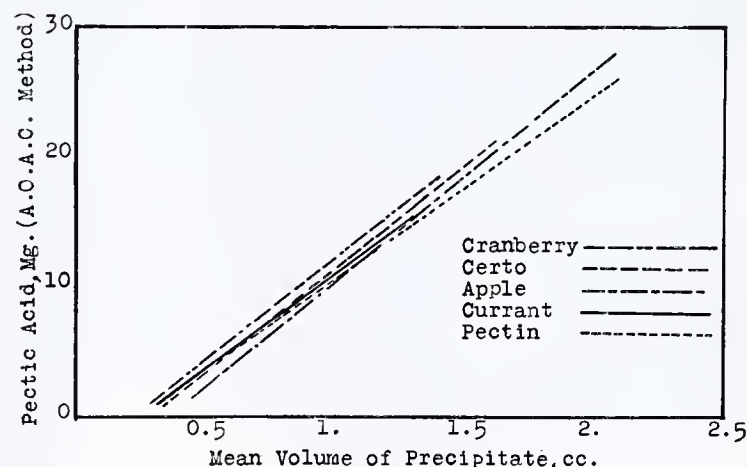


FIGURE 1. RELATION OF VOLUME OF CENTRIFUGAL PRECIPITATE TO PECTIC ACID

The flocculation time varies according to the kind of pectin and the quantity of pectic acid gel in the tubes. Small quantities lose their air bubbles and settle to the bottom in 5 or 6 minutes, whereas dense gels containing much entrapped air require 12 or 15 minutes with occasional stirring with a small glass rod.

Too low results are obtained unless the hot flocculated tubes are cooled before centrifuging. It has been customary to cool to below 25° C.

Various speeds were used on the centrifuge, but optimal results were obtained at 2400 to 2600 r. p. m. in 15 minutes. Results at 1500 or 2000 r. p. m. were always somewhat higher than at 2500. Though 10 minutes in the centrifuge were usually sufficient to give uniform readings, slightly better checks were obtained in 15 minutes, hence this period was adopted. Though a still longer period in the centrifuge gave slightly lower readings, they were no more uniform than at 15 minutes.

Readings should be made within a few minutes after removing the tubes from the centrifuge. There was a tendency for the volume to increase gradually on standing. The best method of taking readings was by holding a finger over the open end of the tube and inverting at eye level. It is essential that tubes be cleaned with chromic acid or other good cleaning solution once a day.

Readings may vary from 0 to 2.0 ml., but best results are obtained at from 0.7 to 1.5 ml. With a little experience one can so regulate the concentration of the pectin solution that the proper amount of precipitate is obtained. Duplicate, or better, triplicate tubes are made and the results averaged.

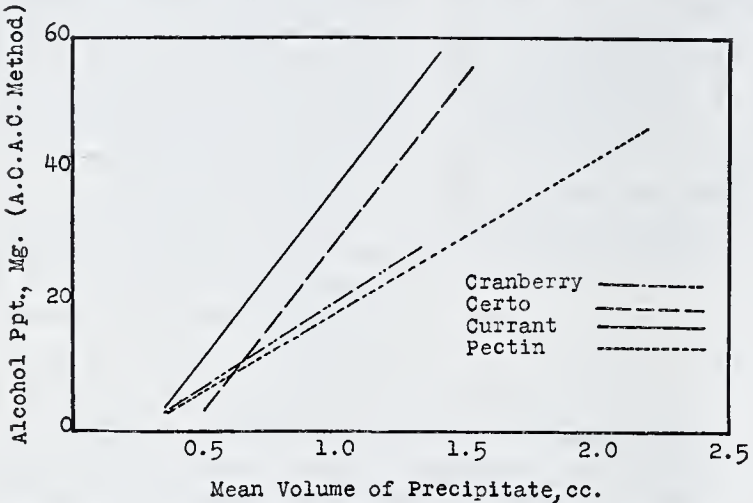


FIGURE 2. RELATION OF VOLUME OF CENTRIFUGAL PRECIPITATE TO ALCOHOL PRECIPITATE (PECTIN)

Within the limits mentioned above, the volume of pectic acid may be correlated with the chemical A. O. A. C. values for pectin or pectic acid. The composition of the precipitate is relatively constant, for Nelson (9) has shown that purified precipitates consist of digalacturonic acid only. Though most fruit juices give similar results, a set of factors should preferably be determined for each type of fruit juice or pectin solution. This is readily done by simply diluting a pectin solution of known strength and noting the corresponding volumes of precipitate. One person can make about twelve determinations in 70 minutes or twenty-four in 2 hours. Only simple equipment and inexpensive chemicals are required for the test. The accuracy of reading is about 0.05 ml., equivalent to 1 to 3 mg. of pectic acid. Occasionally the surface of the precipitate is not perfectly flat. All tubes showing imperfect precipitation should be discarded.

ACCURACY OF RESULTS

Several citrus and apple pectin solutions as well as heat-extracted fruit juices were used so as to have representative types of product. Detailed data were obtained on six different types of solutions and statistically treated. For the sake of brevity only two representative tables are here reproduced, Tables I and II.

TABLE I. ACCURACY OF RAPID CENTRIFUGAL METHOD AS APPLIED TO CITRUS PECTIN SOLUTIONS (A. O. A. C. method used)

No. of DETNS.	VOL. OF JUICE IN SAMPLE	MEAN VOL. OF PPT.	P. E. ^a MEAN	AV. DEVIATION		PECTIN ACID	PECTIN. (ALC. PPT.)
	ML.	ML.	ML.	ML.	%	Mg.	Mg.
12	0.5	0.48	0.0058	0.025	5.2	1.81	2.80
12	1.0	0.70	0.0021	0.025	2.9	3.63	5.60
12	1.5	0.95	0.0072	0.032	3.4	5.44	8.40
12	2.0	1.11	0.0086	0.130	11.7	7.26	11.21
12	2.5	1.31	0.0011	0.040	3.0	9.07	14.00
12	3.0	1.46	0.0095	0.0510	3.5	10.89	16.81
12	3.5	1.66	0.0370	0.160	9.7	12.70	17.60
12	4.0	1.82	0.051	0.230	12.6	14.52	22.42
12	6.0	2.25	0.041	0.180	8.0	21.78	33.60
11	8.0	2.85	0.074	0.310	10.9	29.10	44.80

^a P. E. = probable error.

TABLE II. ACCURACY OF RAPID CENTRIFUGAL METHOD AS APPLIED TO HEAT-EXTRACTED CURRANT JUICE

No. of DETNS.	VOL. OF JUICE	MEAN VOL. OF PPT.	P. E. MEAN	AV. DEVIATION		PECTIC ACID	PECTIN (ALC. PPT.)
	ML.	ML.	ML.	ML.	%	Mg.	Mg.
16	1.0	0.31	0.0047	0.02	6.4	1.48	5.03
16	2.0	0.45	0.0045	0.02	4.4	2.96	10.10
16	3.0	0.60	0.0055	0.024	4.0	4.44	15.10
20	4.0	0.67	0.006	0.035	5.1	5.92	20.10
16	5.0	0.74	0.0066	0.034	4.6	7.40	25.20
16	6.0	0.86	0.0123	0.040	4.7	8.8	30.2
16	7.0	0.92	0.0221	0.042	4.3	10.36	35.2
16	8.0	1.063	0.0333	0.080	7.6	11.84	40.2
4	9.0	1.130	0.0442	0.110	9.7	13.32	45.3
16	10.0	1.22	0.0976	0.044	3.6	14.80	50.3
Av. 5.4							

This method is shown to be reasonably reliable when used on a single type of product. For example, with extracted apple juice, apple pectin, citrus pectin, or pectinous juices of small fruits, the pectic acid content can be closely estimated. The per cent deviation among fifty-five sets of readings varied from 2.9 to 12.6 with mean percentage deviations of from 3.4 to 7.1 in the several products tested. The grand average per cent deviation is 5.5. On the basis of a maximum pectin content in fruits of 2 per cent, the percentage error in using the method will normally be less than 0.1 per cent of pectic acid.

In order to test the personal equation in the method, four independent technicians made tests on a commercial apple pectin extract. The results were mean volumes of precipitate of 1.00 and 1.03, 1.09 and 1.04, 1.07 and 1.01, and 1.06 and 1.015, corresponding to 12.3, 13.4, 13.16, and 13.02 mg. of pectic acid (A. O. A. C. method), respectively. These data indicate that different operators can use the test with a fair degree of accuracy.

Figure 1 shows the relationship between volume of precipitate and weight of pectic acid, Figure 2 the relation of alcohol precipitate to volume of centrifuged pectic acid. By means of similar graphs the pectin content of fruit juices or pectin extracts may be read directly in terms of volume of centrifuged precipitate. In citrus pectin, for example, the ratio of pectic acid to alcohol precipitate was 0.646 to 1, and in heat-extracted currant juice 0.29 to 1.

APPLICATION OF METHOD

The principal application of the rapid centrifugal method for pectic acid is in routine work where large numbers of samples of pectins or pectinous solutions have to be examined in a short time. The results are accurate enough for ordinary control or even routine research work. A few chemical determinations by the A. O. A. C. method should be made from time to time to serve as controls, as it is by this method that the volume of precipitate is translated into terms of weight or per cent of pectin or pectic acids.

Though there may be no definite correlation between volume of precipitate (pectic acid or pectin) and jellifying power of the juice, these determinations are considered to give an approximation of the value of a fruit juice for jelly manufacture, or of the quantity of pectin present in a pectin preparation. Myers and Baker (8) found that the jellifying power of pure pectins was not correlated with their content of pectic acid.

This paper does not seek to establish a definite relationship between volume of pectic acid precipitate, as obtained by this procedure, and jellifying power. Factors such as fruit maturity and extraction methods would probably cause variations to occur. At best, the only really practical method of determining jelly value of pectinous solutions is actually to prepare a series of experimental jellies from an aliquot.

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Determination of Hydroxide and Carbonate in Boiler Waters

I. Methods

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THE determination of the composition of a boiler water involves two fundamental operations, the removal of a representative sample from the boiler, and the accurate analysis of this sample. In discussing the removal of samples from a boiler, the writers have not made a complete survey of current practice but have indicated the conditions which should be fulfilled and have shown a practical sampling system which meets these conditions. In outlining the analytical methods which have been or might be applied to the determination of carbonate, hydroxide, and sulfate in boiler waters, references to important articles have been given but no attempt has been made to include the countless papers in which methods have been endlessly modified or rediscovered.

SAMPLING OF BOILER WATERS

It is still the practice in some plants to collect a sample from a boiler by draining water from a blow-off line or water-column connection into an open vessel. This sample is then cooled, frequently in contact with the air, filtered after the lapse of more or less time, and then analyzed. Such a procedure is obviously worthless for purposes of exact control, even when carried out rapidly. In the first place, the hot solution obtained may have a composition differing widely from that of the boiler water at the time of sampling. Even if it represents the boiler water at the instant of removal, it soon will not, however. During cooling its composition will change owing to re-solution of suspended particles of calcium carbonate, calcium sulfate, or other substances having inverted solubility curves. Moreover, if it is left in contact with the air it will absorb carbon dioxide at a rapid rate, so that a

Titration methods commonly used for the determination of carbonate in boiler waters yield inaccurate values due to uncertainty in end points and error in interpretation. The various methods available for determining carbonate are reviewed. The development and testing of a simple apparatus which gives accurate and consistent results for total carbon dioxide even at very low concentrations is described. Plant tests using a simple but effective method of filtering boiler-water samples at boiler temperature are described, and it is shown that large errors in carbonate, hydroxide, and sulfate may result from poor sampling procedure and the use of inadequate analytical methods.

It is concluded that hydroxide may be determined in boiler water with sufficient accuracy by either the titration with phenolphthalein and methyl orange or the Winkler barium chloride method, but that these methods do not give an accurate value for carbonate.

boiler water which actually contains little carbonate and considerable hydroxide may be reported as showing low hydroxide and high carbonate, or even a considerable concentration of bicarbonate. Such analytical data, when used for control purposes, are dangerous as well as ridiculous.

Better sampling practice at the present time usually consists of cooling the sample under boiler pressure, introducing it directly into a bottle with a ground-glass stopper, filtering immediately in the laboratory, if possible without exposure to the air, and analyzing at once. This procedure eliminates most of the defects previously noted, but it leaves the suspended solids in contact with the water until they are removed by a laboratory filtration which almost always involves exposure of the sample to the air for

several minutes. That even brief exposure may result in high values for carbonate is indicated by Ellms and Beneker (9) and Johnston (18), and proved by the results reported in the third part of the present paper.

The ideal sampling procedure would involve the continuous removal of a small amount of water from the boiler, suspended solids being separated from the sample by means of a filter located within the boiler. The rate of flow and resistance of the filter should be such that no flashing of solution into vapor could take place because of decrease in pressure on passing through the filter. The hot solution free from suspended solids should then pass through a cooling coil maintained under boiler pressure by a throttling valve on the cold discharge side. The continuous stream of cold, filtered boiler water should be introduced at the bottom of a glass-stoppered sampling bottle from which it is allowed to overflow for a few minutes. On removal from the sampling line the bottle should be stoppered at once. Although it is desirable to analyze the sample immediately because of the action of alkaline water upon glass, if bottles or glass-stoppered flasks

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of resistant glass are used, the sample may probably be kept for a considerable time without serious change in composition.

An internal filter combined with external cooling under pressure was first used in connection with boiler waters by Hall, Robb, and Coleman (13), and later by Partridge and White (33), in determining the solubility of calcium sulfate at boiler temperatures; but it is believed that this type of sampling system has never been applied to an operating boiler, largely because of the difficulty of finding a filter medium which would stand up satisfactorily within a boiler, and the difficulty of introducing an internal filter without violating the provisions of the boiler code.

In the third part of this paper there is described a sampling system of rather simple construction which fulfils all the requirements previously noted, although the filter is located just outside the boiler rather than within the boiler drum. This system has demonstrated its practical value in plant service.

SURVEY OF ANALYTICAL METHODS

Accurate knowledge of the carbonate, hydroxide, and sulfate concentrations within a boiler is necessary in any plant where the sulfate-carbonate ratio is controlled to prevent the deposition of sulfate scale,³ and where the sodium sulfate-alkalinity ratio is controlled in an effort to obviate "caustic embrittlement." The routine control methods used in the determination of the stoichiometric concentrations of these ions in boiler water have been inherited by the boiler operator from the investigator interested in the sanitary examination of water supplies. Like many legacies, these methods are rather out of place in their new surroundings, particularly that for the determination of carbonate and hydroxide discussed under the heading of "alkalinity" in the A. P. H. A. Manual (1).

This method, which is the familiar titration with phenolphthalein and methyl orange, and the barium chloride method of C. Winkler⁴ are the only ones which have been used extensively in boiler-water control. Examination of the literature shows a number of other methods which have been, or might be, applied to the determination of carbonate and hydroxide in solutions. A number of these are briefly discussed in the following sections. Only the more important papers dealing with the various methods are noted, for a complete list of the modifications and rediscoveries would contain many hundred items.

The various analytical methods for carbonate may be classified in two main groups, one including methods based on titration of the original sample, the other including methods involving an initial evolution of the carbon dioxide content of the sample.

TITRATION OF ORIGINAL SAMPLE. The methods available for the determination of carbonate and hydroxide in boiler waters by titration of the original sample depend either upon the color change of indicators or upon changes in electrical potential as measuring devices. Any method involving titration of the original sample with the aid of color indicators is subject to the effect of neutral salts upon these indicators, to uncertainty in end points, and to error in interpretation when phosphates, aluminates, silicates, or salts of weak organic acids are present. The large effect of neutral salts upon phenolphthalein is shown by the data of Rosenstein (38) and of Kolthoff (20). Methyl orange, on the other hand, is nearly free from "salt error" (20, 21). On the score of definition of end points in the titration of carbonate-hydroxide solutions,

phenolphthalein again shows less desirable properties than methyl orange. The "sliding end point" of phenolphthalein in such solutions has been noted by Thomson (44), Küster (23), Hildebrand (16), Brubaker (3), and Truog (47). While the methyl orange end point is frequently considered to be uncertain, good precision may be attained by the use of a comparison standard containing the same concentration of indicator and saturated with carbon dioxide, as suggested by Küster in his thorough study (23). The theoretical limit of accuracy in determining the halfway point in the titration of carbonic acid has been estimated by Noyes (32), Tizard and Boeree (45), and Bjerrum (2) as greater than 1 per cent. An error of several per cent would probably be present in most routine analyses of boiler waters. The utmost care in titration technic would be of no avail, however, if part of the effect attributed to carbonate by the ordinary method of interpretation were actually due to the presence in the boiler water of ions of acids with dissociation constants in the same range as those of carbonic acid. The use of indicators other than phenolphthalein and methyl orange obviously offers little chance of improvement in accuracy.

As far back as 1897 Küster concluded that the titration with phenolphthalein and methyl orange was not an accurate method for determining carbonate in carbonate-hydroxide solutions. After a painstaking investigation he recommended the Winkler barium chloride method for the determination of hydroxide, and the titration with methyl orange for the determination of total alkali. In searching for an accurate method for the control of boiler-water conditioning with soda ash, Hall (12) discarded the phenolphthalein-methyl orange titration because it gave high values for carbonate which he attributed to the presence in the boiler waters of salts of weak organic acids. He adapted the Winkler barium chloride method by using phenolphthalein as indicator in the titration of duplicate samples, to one of which barium chloride was added to precipitate carbonate. Experiments by McKinney (15, 30) question the accuracy of this method for carbonate, and Larson (24) has recently announced that it yields unreliable carbonate values in the presence of sulfate. Poethke and Manicke (36) in their very complete investigation of the Winkler barium chloride method found that the phenolphthalein used as indicator was very readily removed from solution by adsorption on the precipitate of barium carbonate. When the method is applied to a water containing sulfate, it is possible that the barium sulfate precipitated with the barium carbonate may remove the indicator from solution so rapidly as to prevent the satisfactory location of the titration end point. The error introduced by the use of the Winkler method on solutions containing sulfate has been independently observed by the present writers and is discussed in the second part of this paper.

The excess-acid method was apparently first used with phenolphthalein by Warder (53). Its application in connection with water softening is mentioned by Handy (14), and Hall (11) compared it with the phenolphthalein-methyl orange titration and modified Winkler method for the determination of carbonate in boiler waters. Hall's data show that the values obtained with the excess-acid method were quite consistently somewhat lower than those from the other titrations. In the light of present knowledge, this may indicate that the excess-acid method yields more accurate results for carbonate in boiler waters than either the phenolphthalein-methyl orange titration or the modified Winkler method. Further investigation seems justified.

Electrometric titration has not, to the writers' knowledge, been applied to actual boiler-water analysis, although Hildebrand (16), Greenfield and Buswell (10), and Davis, Oakes, and Salisbury (8) obtained satisfactory breaks in their titration curves for sodium carbonate solutions. Cox (7), using a

³ Where phosphate is used as a conditioning chemical, the PO_4 concentration must similarly be known.

⁴ The writers have been unable to procure a copy of Winkler's "Massanalyse," in which this method was first described. For discussion of the method, see Küster (23).

differential method, located the end points more definitely. Zhukov and Gortikov (57), also using the differential method, found that small amounts of carbonate showed up clearly in the titration of sodium hydroxide, so that this method may have some promise for use on boiler waters not containing phosphate, aluminate, silicate, or similar ions in amounts sufficient to prevent interpretation of the titration curve. The potentiometric method has also been applied to carbonate-hydroxide mixtures by Little and Durand (28), whereas Kolthoff (22) found the conductimetric method usable within limits.

The method recently suggested by McKinney (30) for the determination of carbonate by titration between definite pH values and the application of dissociation data is subject to the errors of any other titration method if the pH reference levels are determined colorimetrically. More accurate measurement of pH by the electrometric method in the control of boiler-water conditions is quite possible, but to date this method has not been applied outside of a few special investigations.

McKinney's proposal to calculate hydroxide concentrations from pH measurements is perfectly logical, but since the pH value of most boiler waters is close to or above 11, and since colorimetric methods employed in a routine manner will frequently not yield values accurate to within 0.2 unit, the hydroxide values calculated from such measurements will be only approximate. Electrometric measurement of pH here again offers increased accuracy.

EVOLUTION OF CARBON DIOXIDE FROM SAMPLE. The total carbon dioxide content of a solution may be determined in a variety of ways, all of which depend upon the initial evolution of the carbon dioxide from the original sample. The various methods utilize measurement of gas pressure or volume, the freezing-out of solid carbon dioxide, and absorption in various solid or liquid media. Many of these methods have been developed in fields rather distant from boiler-water chemistry. Their possible application to the latter depends upon how simply and how accurately they may be used for the determination of the small amounts of carbon dioxide present in boiler waters.

The absorption of carbon dioxide in potassium or sodium hydroxide is old enough to pass for a tradition. Petterson and Palmquist (35) adapted this process to the determination of the small carbon dioxide content of air by measuring the volume of a sample before and after absorption of carbon dioxide. L. W. Winkler (54) translated the gas-volumetric method to the realm of solutions, Van Slyke (48) added the use of vacuum to remove the carbon dioxide from the solution without heating, and McClendon (29) extended the use of Van Slyke's apparatus to the determination of the total carbon dioxide in sea water. Further applications of the general method to solutions were made by Shaw (41) and Hall (11), the latter being specifically interested in boiler waters. Van Slyke and Neill (49) also developed a manometric method to measure the carbon dioxide evolved from a sample.

Determination of carbon dioxide by freezing it out from a gas mixture has been used by Theis in solid-gas equilibrium studies (43). Yensen (56) also used this method with subsequent expansion of the carbon dioxide into a known volume whose pressure was measured.

The determination of evolved carbon dioxide by absorption offers an embarrassing variety of media and methods. The use of solid absorbents in connection with the determination of carbon in steel has become so well standardized that it need not be discussed. The problem here, as in the use of potassium hydroxide for absorption in weighing bottles, is to remove all of the carbon dioxide from the gas stream without gain or loss of water in the absorption unit which is weighed.

L. W. Winkler (55) avoided heating his water samples by using hydrogen generated in them by the action of acid on zinc to sweep the carbon dioxide into the absorption bulb. Waggaman (51) has described an arrangement which might prove applicable to boiler-water analysis. Absorption methods involving determination of carbon dioxide by titration seem, however, to be more generally applicable to boiler-water control than gravimetric methods.

When potassium or sodium hydroxide is used as an absorbent, the subsequent titration of the carbonate-hydroxide mixture will be more accurate if the barium chloride method of C. Winkler is used to determine residual hydroxide than if the titration is made with phenolphthalein and methyl orange, owing to the uncertainty in the phenolphthalein end point in the latter case.

The advantages of replacing potassium or sodium with calcium hydroxide, or better still, barium hydroxide, have been periodically rediscovered for the past century, if it is true that Dalton originated the method, as claimed by Letts and Blake (26). The latter investigators made a comprehensive survey of the method, which is usually associated with the name of Pettenkofer (34). They concluded that the barium carbonate precipitate produced by absorption of carbon dioxide should not be removed by filtration, but that the residual barium hydroxide should be titrated in the presence of the precipitate with phenolphthalein as an indicator. Nearly all of the possible variations of the methods have been tried. J. Walker (52), Nishi (31), and Johnston and A. C. Walker (19) have preferred to filter out the barium carbonate precipitate before titrating the excess barium hydroxide. J. R. Cain (4) and Schollenberger (39), on the other hand, recovered the barium carbonate, the former titrating it with methyl orange as indicator, the latter weighing it. In general, however, titration of the residual barium hydroxide without removal of the barium carbonate has been found satisfactory (26, 27, 47). When acids other than carbon dioxide may be absorbed also, it is possible to titrate both the residual barium hydroxide and the precipitated barium carbonate. An entirely different method of measurement was used by Itano (17), who determined the amount of carbon dioxide absorbed by the decrease in the conductivity of the barium hydroxide solution. Spolr and McGee (42) and Raymond and Winegarten (37) have also adopted this method. Lindner (27) has pointed out possible sources of error in the barium hydroxide absorption, whereas Schollenberger (40) has stated that thymolphthalein yields a sharper end point than phenolphthalein in the titration of the excess adsorbent.

Many devices have been used to insure complete absorption of carbon dioxide in the barium hydroxide solutions used. Vesterberg (50) found that a 10-bulb tube was satisfactory. Truog (47) devised a simple and very ingenious scrubbing tower. T. L. B. Cain (5) added gelatin to his barium hydroxide solution to increase the time of retention of gas bubbles at its surface. It was left for Constantino (6) to make the important improvement of circulating a small volume of gas through a closed system containing two flasks, in one of which the carbon dioxide was evolved from the sample, and in the other it was absorbed in barium hydroxide. Lescoeur and Manjean (25) subsequently used the same idea.

The accuracy attainable in the measurement of small quantities of carbon dioxide by absorption in barium hydroxide and titration of the excess absorbent has attracted many investigators in widely different fields of research. In searching for an accurate means of determining carbonate concentrations in boiler waters, the writers saw more promise in this method than in any of the others noted. This led to the development of two types of apparatus which are described in the second part of this paper.

II. Development and Testing of Apparatus for Carbonate Determination by Evolution and Absorption in Barium Hydroxide

TWO pieces of apparatus were designed by the writers for the determination of carbonate in boiler waters.

The first of these was used in the laboratory in connection with work on an experimental boiler, the results of which will be reported in another paper. The second apparatus, which was both simpler and more accurate, was subsequently developed for the plant-control tests described in the third part of the present paper. The fundamental idea was the same in both cases. The total carbon dioxide content of a water sample was liberated by addition of excess acid and heating, and this carbon dioxide was carried by an air stream into an excess of standard barium hydroxide, precipitating barium carbonate. The residual barium hydroxide was then titrated with standard acid.

The successful application of this method to the determination of carbonate in solution depends upon the following factors: (1) complete removal of all carbon dioxide from the sample; (2) complete absorption of liberated carbon dioxide in barium hydroxide; (3) complete precipitation of barium carbonate equivalent to carbon dioxide liberated and absorbed; (4) titration of residual barium hydroxide to a definite reproducible end point; and (5) freedom from contamination by carbon dioxide of the atmosphere. The ways in which these conditions were met will be discussed in connection with the description of each piece of apparatus. In general, the second condition is the one least likely to be satisfied by ordinary apparatus. Since it is necessary to sweep the carbon dioxide out of the original sample by means of an air stream initially free from carbon dioxide, a considerable volume of gas must be passed through whatever absorbing unit is used. As a bubble of gas containing carbon dioxide on passing through barium hydroxide immediately forms a film of barium carbonate at the gas-liquid interface, it is highly improbable that complete absorption can be attained except by prolonged contact or intimate mixing.

Since the absorption method determines only the total carbon dioxide in the sample, it must be combined with one of the ordinary titration methods if a value for hydroxide is also desired. In designing the apparatus for the absorption method, provision was therefore made for carrying out either the standard titration with phenolphthalein and methyl orange, or the Winkler barium chloride titration on the sample before determining the total carbon dioxide.

FIRST ABSORPTION APPARATUS

The method of operation of the first absorption apparatus, shown in Figure 1, is as follows: Air is first pumped through the apparatus for 10 minutes by the aspirator. Towers A and B, which are filled respectively with soda lime and barium hydroxide, free the entering air from carbon dioxide so that the pumping operation removes all of this gas from the system. Flask D, which is used to contain the sample, is quickly

removed and stoppered. The measured sample is then introduced into this flask and it is replaced on the apparatus as quickly as possible to prevent contamination by atmospheric carbon dioxide. The sample is then titrated in this flask with standard 0.05 N or 0.1 N hydrochloric acid to the phenolphthalein and methyl orange end points, or if the Winkler barium chloride method is being used, to the phenolphthalein end point alone. After this titration, excess hydrochloric acid equivalent to 2 cc. of normal acid is added to the sample through tube M, and air is slowly pulled through the sample and through flask E and tower K, each of which contains part of a measured amount of standard barium hydroxide. At the same time the sample is heated to boiling by the

heater C. The air sweeps the carbon dioxide from the heated acid solution into the barium hydroxide where it is removed as a precipitate of barium carbonate. The barium hydroxide in K is then drained into E, and K is washed up and drained down repeatedly with carbon dioxide-free water introduced in funnel L. Phenolphthalein is added with the last portion of wash water. The excess hydroxide in E is then titrated with standard acid from

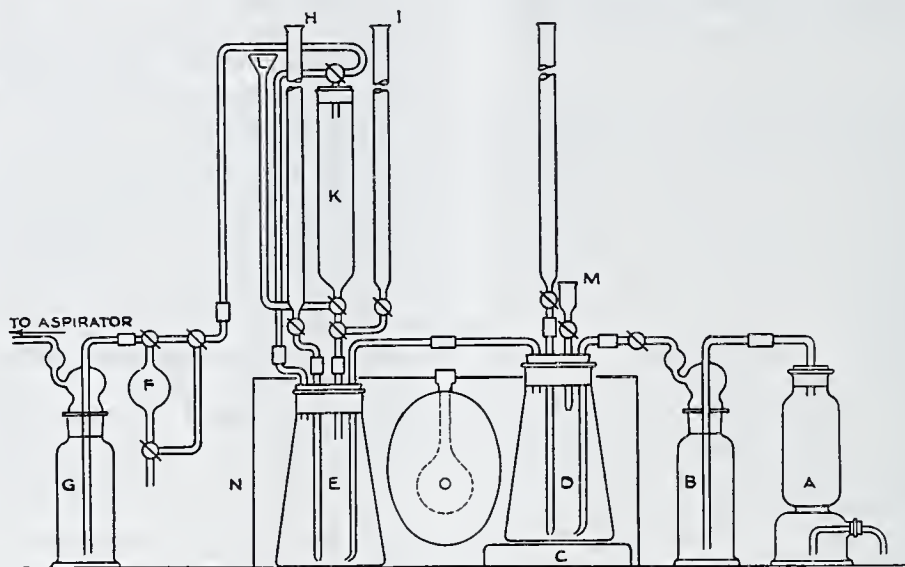


FIGURE 1. ARRANGEMENT OF FIRST APPARATUS

buret H to the disappearance of the last trace of color. The difference between this end point and the acid equivalent of the hydroxide used in the tower and flask gives the acid equal to the total carbon dioxide in the sample.

The bulb F at the end of the absorption system is a sight bulb which is filled with a saturated solution of barium hydroxide. During the absorption of the carbon dioxide from the sample, the gas leaving the apparatus is passed through this bulb. If for any reason some of the carbon dioxide is not removed in the absorption system, the saturated barium hydroxide in the bulb becomes cloudy, indicating that some of the gas is escaping and that the results of the analysis will not be correct. G is a guard bottle containing barium hydroxide. N is a box painted white on the inside and equipped with a daylight bulb and a reflector, O. Flasks D and E are contained in this box so that all titrations are carried out with the same constant illumination. I is a buret from which the barium hydroxide is measured out into E and K. The authors customarily used 50 cc. of approximately 0.02 N barium hydroxide, about 30 cc. being run into K and the remainder into E. The excess of barium hydroxide remaining after absorption was titrated with 0.02 N hydrochloric acid. The barium hydroxide was initially saturated with respect to barium carbonate.

In this system complete removal of carbon dioxide from the acidified and heated sample could be insured by passing the air stream through it for a sufficiently long time. A period of 15 minutes was found to be ample for solutions containing up to 90 parts per million carbonate. Practically complete absorption of the liberated carbon dioxide was insured by passing the gas stream first into barium hydroxide in E and

then through *K*, which was 30 cm. high, 3 cm. in diameter, and was filled with 3-mm. glass beads. The rate of flow of air was about 5 bubbles per second from the tip in *E*. By carrying out the titration of the excess barium hydroxide with constant illumination, closely reproducible results were obtained. Blank tests indicated that all carbon dioxide was scrubbed from the entering air by passing through *A* and *B*. Further blank tests showed that hydrochloric acid could be used for acidifying the sample without danger of carrying over acid in the gas stream to the barium hydroxide.

The accuracy of the apparatus was tested and the method was compared with both the standard phenolphthalein-methyl orange and the modified Winkler barium chloride titrations, using samples prepared from standard solutions of pure sodium carbonate and pure sodium hydroxide. The standard carbonate solution was prepared by heating c. p. sodium bicarbonate in a jacketed crucible at 270° to 300° C. for 30 minutes, weighing out a given amount of the sodium carbonate formed, and diluting to the desired volume with distilled water. The sodium hydroxide solution was prepared by adding c. p. sodium metal to water protected from the atmosphere by a layer of ether. The ether was then evaporated and the concentration of the hydroxide determined by titration with hydrochloric acid. This gave a sodium hydroxide solution which was carbonate-free. Both standard solutions were kept in paraffined bottles. The necessary volumes of the standard solutions were added to distilled water to make up 200-cc. samples of the desired concentrations. The distilled water used in making up these samples contained some carbon dioxide which was determined by the absorption method to be equivalent to 6 parts per million carbonate. This constant carbonate concentration in the distilled water is included in the known concentrations shown in the subsequent tables.

TITRATIONS WITH PHENOLPHTHALEIN AND METHYL ORANGE. The values obtained with a series of hydroxide-carbonate samples titrated by the standard method using phenolphthalein and methyl orange are shown in Table I.

TABLE I. TESTS OF STANDARD TITRATION WITH PHENOLPHTHALEIN AND METHYL ORANGE ON SOLUTIONS OF KNOWN COMPOSITION

REFERENCE No.	HYDROXIDE		CARBONATE	
	Known P. p. m.	Found P. p. m.	Known P. p. m.	Found P. p. m.
1	55	47	6.0	24.7
2	55	45	6.0	29.7
3	81	77	6.0	9.1
4	81	66	26.1	31.3
5	81	78	46.1	47.9
6	81	77	86.2	89.0
7	191	188	26.1	31.6
8	191	187	46.1	53.9
9	191	189	46.1	53.9
10	285	277	6.0	16.5
11 ^a	285	277	6.0	19.0
12 ^a	285	276	26.1	34.9
13 ^a	285	277	46.1	57.0
14	285	284	86.2	85.5
15 ^a	407	411	6.0	0.0
16	407	403	6.0	11.1
17 ^a	407	403	6.0	6.4
18 ^a	407	398	26.1	34.8
19 ^a	407	400	46.1	47.6
20 ^a	407	395	86.2	101.2

^a Calcium sulfate added in solution.

The titrations were carried out in flask *D* of the apparatus shown in Figure 1 under conditions superior to those usually surrounding control titrations of boiler waters. Loss of carbon dioxide was obviated by introducing the acid slowly near the bottom of the flask which was agitated only by a gentle swirling motion. The values calculated for carbonate by the customary method of interpretation (*1*) are, however, consistently high and rather irregular, particularly for the lower concentrations. As a result of the arbitrary method of calculation, high values for carbonate lead to slightly low values for hydroxide.

The titrations shown in the table were made on distilled-water solutions containing no impurities. In the analysis of boiler waters it is doubtful if the relative accuracy shown here could be expected, since salts of slightly dissociated acids other than carbonic acid may be present, the neutral salt content is generally much higher, and the solutions are in the main more or less colored.

TITRATIONS BY MODIFIED WINKLER BARIUM CHLORIDE METHOD. The results of titrations by the modified Winkler barium chloride method on a series of samples of known concentration are shown in Table II.

TABLE II. TESTS OF BARIUM CHLORIDE TITRATION ON SOLUTIONS OF KNOWN COMPOSITION

REFERENCE No.	PROCEDURE IN TITRATION	HYDROXIDE		CARBONATE	
		Known P. p. m.	Found P. p. m.	Known P. p. m.	Found P. p. m.
1	(1)	81	86	26.1	0.0
2	(1)	81	90	46.1	3.3
3	(1)	81	101	86.2	5.0
4	(1)	191	194	26.1	9.5
5	(2)	191	188	26.1	31.6
6 ^a	(2)	191	188	26.1	34.8
7	(3)	191	190	26.1	26.9
8	(4)	191	186	26.1	41.2
9 ^a	(4)	191	182	26.1	53.9
10 ^a	(3)	191	186	26.1	41.2
11	(2)	191	189	46.1	49.1
12	(5)	191	189	46.1	49.1
13	(6)	191	192	46.1	39.6
14	(1)	191	193	46.1	36.4
15	(1)	191	196	46.1	23.8
16 ^a	(2)	191	187	46.1	55.5
17 ^a	(3)	191	186	46.1	61.7
18 ^a	(4)	191	183	46.1	71.4
19	(3)	191	190	46.1	46.0
20	(1)	285	290	26.1	0.0
21 ^a	(1)	285	292	46.1	6.3
22	(1)	285	308	86.2	0.0

(1) 10 cc. of 0.2 *N* BaCl₂ added, sample titrated immediately.

(2) 10 cc. of 0.2 *N* BaCl₂ added, sample boiled, titrated hot.

(3) 10 cc. of 2 *N* BaCl₂ added, sample titrated immediately.

(4) 10 cc. of 2 *N* BaCl₂ added, sample boiled, titrated hot.

(5) 10 cc. of 0.2 *N* BaCl₂ added, sample boiled, titrated cold.

(6) 10 cc. of 0.2 *N* BaCl₂ added, sample let stand 1 hour, then titrated.

^a Solution of calcium sulfate used to make sulfate concentration of sample about 700 parts per million.

These samples were treated in a variety of ways as indicated by the number in the column headed "Procedure in Titration." In the case of the first method, in which 10 cc. of 0.2 *N* barium chloride were added and the sample titrated immediately, it is seen that the values for carbonate are consistently far too low. This is undoubtedly due to the fact that not enough excess of barium chloride was added to produce rapid and complete precipitation. In fact, even in some of the samples containing fairly high carbonate concentrations, no precipitate could be seen on the addition of the barium chloride. These tests were all made at room temperature.

In the case of the second method of treatment, where 10 cc. of 0.2 *N* barium chloride were added and the samples boiled for a few seconds and then titrated hot, the values are seen to be much closer to the known concentrations than in the previous case. Here, however, they are in general high, particularly for those samples which contained calcium sulfate. The amount of barium chloride added to numbers 6 and 16 was not more than enough to precipitate the sulfate, leaving none for the carbonate. This would mean that the carbonate in the solution would be titrated in almost exactly the same manner as in the sample to which no barium chloride has been added. As a result, the calculations for these samples should have shown almost no carbonate rather than values higher than the known concentrations. The conclusion that the sulfate seriously interferes with the titration is inescapable.

The third method, that in which 10 cc. of 2 *N* barium chloride were added and the sample immediately titrated, gave accurate results on numbers 7 and 19. When calcium sulfate

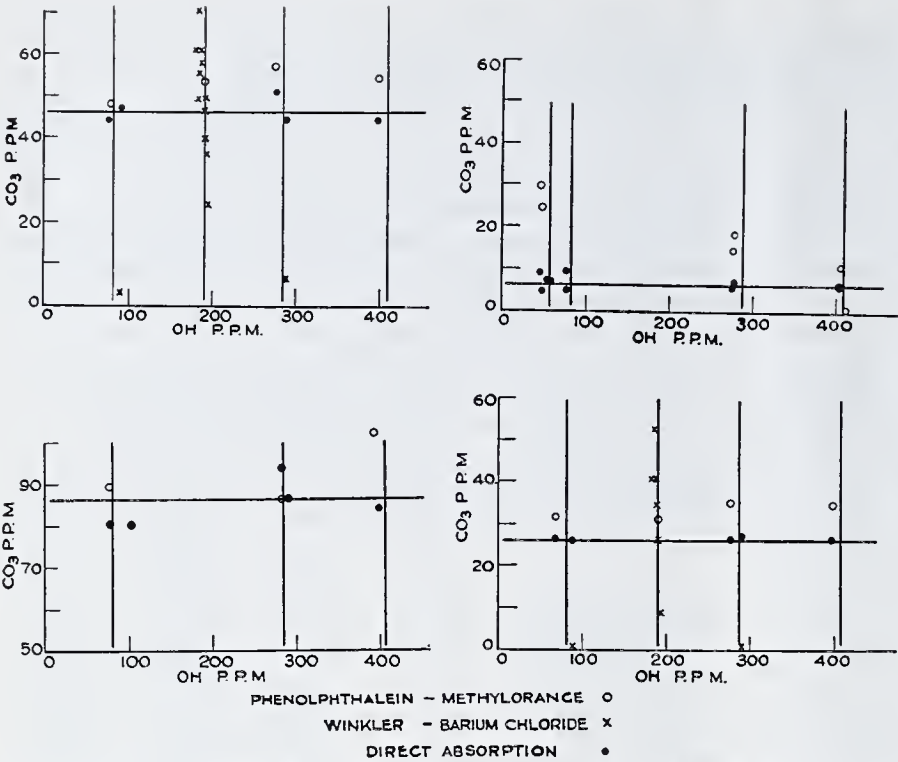


FIGURE 2. COMPARISON OF RESULTS OBTAINED BY VARIOUS ANALYTICAL METHODS ON HYDROXIDE-CARBONATE SOLUTIONS OF KNOWN COMPOSITION

was introduced into the samples as in numbers 10 and 17 the results were again too high.

The fourth method, in which 10 cc. of 2 N barium chloride were added and the sample boiled for a few seconds and titrated hot, gave high results. The presence of calcium sulfate increased the error.

Two other methods of treating the samples were tried as indicated in Table II. Since they were rather inconvenient and demanded considerable time, and furthermore because they did not seem to offer any greater accuracy than some of the other methods, they were not investigated further.

TABLE III. TESTS OF DIRECT ABSORPTION METHOD ON SOLUTIONS OF KNOWN COMPOSITION

REFERENCE NO.	CARBONATE	
	Known P. p. m.	Found P. p. m.
1	6.0	5.7
2	6.0	5.7
3	6.0	4.5
4	6.0	6.4
5	6.0	7.1
6	6.0	4.4
7	6.0	9.6
8	6.0	5.8
9 ^a	6.0	6.5
10	6.0	6.8
11 ^a	26.1	26.7
12	26.1	25.2
13 ^a	26.1	25.6
14	26.1	27.7
15 ^a	26.1	25.6
16	46.1	43.8
17	46.1	47.5
18 ^a	46.1	51.0
19 ^a	46.1	43.8
20 ^a	46.1	43.9
21	86.2	80.0
22	86.2	80.0
23	86.2	93.6
24	86.2	86.3
25 ^a	86.2	83.5

^a Calcium sulfate added to the sample in solution.

In general the barium chloride titration will yield the best results when an appreciable excess of the chloride is used. Letting the sample stand or heating it before titration does not increase the accuracy. When a considerable amount of sulfate is present in the solution, the barium chloride titration gives high values for carbonate and, consequently, slightly low values for hydroxide.

DIRECT ABSORPTION METHOD FOR CARBONATE.
The results of the direct absorption method for the determination of carbonate are shown in Table III. These results are very close throughout the entire range of concentrations investigated, the method is accurate at low carbonate concentrations, and the presence of calcium sulfate introduces no error. It is to be expected that the presence of most impurities would have little effect when it is remembered that the actual titration for the carbonate is conducted in a distilled-water solution containing only barium hydroxide and suspended barium carbonate resulting from the absorption of carbon dioxide evolved from the original sample.

The results of all of the determinations by the various methods are shown graphically in Figure 2. The heavy horizontal lines indicate the known carbonate concentration of the samples, and the heavy vertical lines, the known hydroxide for the samples plotted close to them.

Although the results shown in Tables I to III and Figure 2 by no means represent a complete study of the three methods tested, they do show that even with uncontaminated solutions under the optimum conditions of experimentation neither the

standard titration with phenolphthalein and methyl orange nor the modified Winkler barium chloride method is consistently satisfactory for the estimation of small concentrations of carbonate in the presence of hydroxide up to 400 parts per million hydroxide. With actual boiler waters under ordinary routine analytical conditions, the results may be expected to be much less exact. Even when working with relatively uncontaminated⁵ water in an experimental boiler, the writers found tremendous discrepancies between the carbonate concentrations indicated by the ordinary interpretation of the phenolphthalein-methyl orange titration and those found by the direct absorption method. Table IV presents a comparison of values for carbonate obtained by the two methods for four successive samples of water taken at intervals of one day from an experimental boiler during a scale-formation test.

TABLE IV. CARBONATE DETERMINATIONS BY TWO METHODS ON WATER FROM AN EXPERIMENTAL BOILER

PHENOLPHTHALEIN-METHYL ORANGE TITRATION		DIRECT ABSORPTION Carbonate P. p. m.
Hydroxide P. p. m.	Carbonate P. p. m.	
102	88	12
109	64	11
108	71	10
111	60	11

In contrast to the uncertain results obtained with the customary titration methods, the absorption method for total carbon dioxide shows consistent results, particularly in the case of the lower concentrations of carbonate, and it may be expected to serve as satisfactorily for actual boiler waters as for pure solutions. The only source of possible misinterpretation of the results would be the presence in the boiler water of sulfides, sulfites, or some organic salts which might yield a volatile acid in the direct absorption determination.

As carried out in the apparatus of Figure 1, the chief disadvantages of the absorption method are the complicated apparatus and the time required, which is approximately 1 hour for each sample.

⁵ This water contained a small concentration of aluminate resulting from the attack of the alkaline solution on an alundum filter used within the boiler at the time.

IMPROVED ABSORPTION APPARATUS

The disadvantages of the absorption method just described arose from the complicated apparatus used. An effort at simplification resulted in the development of an improved apparatus which requires a relatively short time for an analysis of total carbon dioxide and which may be operated satisfactorily by a person not familiar with the chemistry of the process or skilled in the manipulation of apparatus.

The essential difference between the original and the simplified absorption apparatus is the manner in which the carbon dioxide is absorbed. In the simplified equipment the sample flask and the absorption flask form a closed system in which the air containing carbon dioxide is circulated continuously by a small pump until absorption is complete, thus eliminating the need for a scrubbing tower on the absorption flask. Absorption is hastened by the use of a device to produce many small bubbles in the absorption flask, although this is not essential to the satisfactory operation of the apparatus.

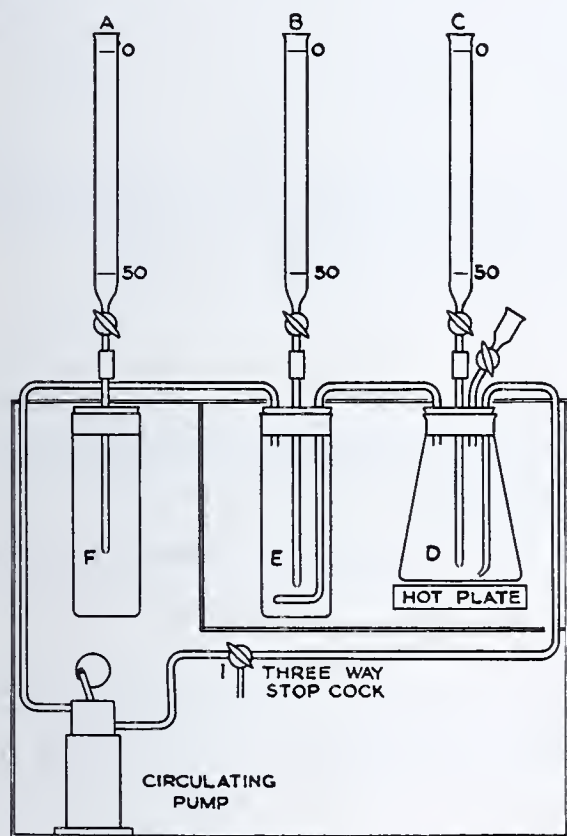


FIGURE 3. IMPROVED APPARATUS

The apparatus consists of a box equipped with daylight bulbs and a ground-glass panel for even illumination. Inside the box are fastened three stoppers connected to the burets and air-circulating system as shown in Figure 3. The evolution flask *D* containing the sample is attached to the right-hand stopper and is supported in place by a small hot-plate which is swung up beneath it. The absorption tube *F* is filled with 0.03 *N* barium hydroxide from the buret on the left-hand stopper, and is then attached as at *E* to the middle stopper for the absorption and subsequent titration.

The air outlet from the absorption tube *E* is connected directly to the suction side of a small air pump. The delivery side of the pump is connected back to the sample flask *D*, as shown. The air line from the pump to this flask is provided with a three-way stopcock with one connection open to the atmosphere to make it possible to vent air from the system before and after an absorption in order to relieve pressure differences. The bubbling device shown inside the absorption tube is a perforated platinum disk sealed in glass.⁶ The

⁶ Supplied by the Fisher Scientific Company.

purpose of this disk is to break up the gas stream into fine bubbles so that the carbon dioxide may be rapidly absorbed by the barium hydroxide. A small air condenser, not shown in Figure 3, is placed between *D* and *E* to prevent condensate from *D* from collecting back of the disk on the bubbling device and stopping the air flow. The circulating pump, which may be driven by any convenient means, consists of two sliding sleeves sealed with mercury to prevent the possibility of any air escaping.

The supply bottles for acid and barium hydroxide are mounted on a shelf formed by the projecting base of the box, and are connected to the burets, *A*, *B*, and *C*, by glass tubes. Rubber bulbs are also connected to the supply bottles to allow rapid filling of the burets by air pressure. Excess acid above the zero mark of the buret is automatically siphoned back into the supply bottle on release of pressure.

The operation of this apparatus is extremely simple. The measured sample is placed in flask *D*, phenolphthalein is added, the flask is placed on the apparatus, and the heater lifted into position as shown. The absorption tube is filled with 0.03 *N* barium hydroxide from buret *A* as at *F*, and is then put in position at *E*. The sample in *D* is titrated to the phenolphthalein end point with 0.1 *N* hydrochloric acid. Methyl orange is then added to the sample through the small tube shown at the top of *D*, and the sample is titrated to this second end point. Titration with either phenolphthalein or methyl orange is necessary to give a value for hydroxide; by using both indicators a comparison value for the carbonate may be calculated if desired. Excess hydrochloric acid equivalent to 2 cc. of normal acid is then added to the sample, and it is heated just to the boiling point. The carbon dioxide evolved from the sample is swept by the circulating air into the barium hydroxide where it is precipitated as barium carbonate. During a 10-minute absorption period, the gas is passed through the hydroxide about 15 times, insuring practically complete absorption. The excess hydroxide in *E* is then titrated, the phenolphthalein used as indicator being contained in the 0.03 *N* acid added. From the acid equivalent of the hydroxide originally introduced into tube *E* and the amount of acid used for the final titration, the amount of carbon dioxide evolved from the sample is calculated. In alkaline solutions whose pH is in the range above 11, the total carbon dioxide as determined by the absorption method may be assumed to be equivalent to the carbonate concentration of the solution. For less alkaline solutions, the concentrations of carbonate and bicarbonate may be calculated conveniently from the total carbon dioxide and pH by the method outlined by McKinney (30).

TABLE V. RESULTS OF ANALYSIS OF SOLUTIONS OF KNOWN CARBONATE CONCENTRATION BY MEANS OF IMPROVED ABSORPTION APPARATUS

CARBONATE	
Known <i>P. p. m.</i>	Found <i>P. p. m.</i>
8.8	8.6
	8.8
22	21.6
	22.0
44	42.0
	42.5
87	83
	82

Eight samples of known concentration prepared from pure standard sodium carbonate solution were analyzed in the manner described. The results, as shown in Table V, were very consistent and considerably more accurate than were the results obtained on the more complicated apparatus shown in Figure 1.

The standard sodium carbonate solution used in this series was made up with double-distilled water which had been

boiled for 20 minutes and cooled in a flask protected from carbon dioxide by ascarite. The water used in diluting given volumes of the standard carbonate solution to the standard volume of 200 cc. was also prepared from double-distilled water boiled and cooled in the same manner. Blank runs in the absorption apparatus on samples of water prepared in this manner showed it was free of carbon dioxide. These precautions were taken to obviate the necessity of adding a carbonate correction for the distilled water used in making up the standard solution. It was also desired to determine whether, at low concentrations of carbonate, all of the carbonate was evolved from the solution. The extremely good checks obtained at the low concentrations indicated that all the carbonate was evolved.

It is interesting to note that the barium hydroxide used in this simplified apparatus may be standardized in such a manner as to correct for the carbon dioxide in the system at the start of a determination. This is done by filling the absorption tube with the volume of barium hydroxide it is desired to use, then putting distilled water, carefully freed of all carbon dioxide and equal in volume to the samples to be analyzed, in the evolution flask, circulating the air through the system for 10 minutes, and titrating the barium hydroxide with the standard acid. The acid equivalent of the hydroxide thus obtained is a value corrected for any carbon dioxide initially present in the system. This procedure was followed in the analysis of the solutions shown in Table V, and also in

the analysis of the boiler-water samples referred to in the third part of this paper.

Tests were also run with varying periods of boiling the sample and with varying amounts of excess acid up to 4 cc. of normal hydrochloric acid added to a 200-cc. sample to determine whether any acid might be carried over into the barium hydroxide. In no case could any effect be measured.

The results obtained in the direct absorption determination are probably more accurate than those given by any standard titration method, especially when applied to impure waters. The improved apparatus is not complicated, and may be satisfactorily operated by an inexperienced person. Although approximately 20 minutes are required for one complete determination, in many cases it would seem better for control purposes to have a single accurate analysis than any number which cannot be relied upon.

It should be remembered that the absorption apparatus yields a value only for the total carbon dioxide present in a sample of water, regardless of the form in which it may exist in solution. Where precision is necessary in experimental work, the activities or concentrations of bicarbonate and carbonate in the original sample may be calculated from the dissociation constants of carbonic acid. For practical purposes the total carbon dioxide content of the alkaline water from a boiler may usually be assumed to have been present in that water as carbonate, although in the case of natural waters in contact with the air such an assumption would lead to highly inaccurate conclusions.

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III. Plant Tests of Various Methods for Determining Ratios for Boiler-Water Control

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SUBSEQUENT to the development and laboratory testing of the simplified absorption apparatus for the determination of total carbon dioxide, a series of boiler-water tests was carried out on one of the 125-pound W-type Stirling boilers in the Congress Street Heating Plant of the Detroit Edison Company. The make-up of this plant is nearly 70 per cent, the remaining 30 per cent being condensate returned from the customers' heating systems. Detroit city water is used for make-up and the total boiler input is passed through a feed-water heater and live-steam purifier, where part of the carbon dioxide content is removed with a corresponding precipitation of some calcium carbonate. Soda ash is added continuously by a proportioning device to the water as it goes to the heater. As a result of the rapid hydrolysis of carbonate in the boiler water, the latter contains a low concentration of carbonate and a relatively large concentration of hydroxide.

The tests had three objectives: the comparison of results obtained by filtration in the sampling line at boiler temperature with those obtained by filtration of the cooled sample in the laboratory; the comparison of the values for carbonate, hydroxide, and sulfate obtained by various methods, and of the values for the sulfate-carbonate and sodium sulfate-alkalinity ratios resulting from the use of these different methods; and the comparison of boiler-water concentrations in the upper and lower drums of a boiler steaming at normal rating.

SAMPLING SYSTEM

It was stated in the first part of this paper that filtration of samples of boiler water at boiler temperature was desirable. One of the difficulties with such a procedure is the rapid disintegration of many filter media under the rather severe conditions of contact with an alkaline solution at an elevated temperature. Filters of cloth supported on wire disappeared completely during runs with an experimental boiler, whereas alundum tubes disintegrated in a period of several days. A small filter consisting of fine-mesh copper screen wrapped in several layers on a perforated pipe finally solved the problem of filtration in the experimental boiler, the suspended particles in the boiler water being trapped between the layers, thus forming their own filter medium. Such a system is fundamentally correct as long as the character of the solid phases in the boiler does not vary.

Since it did not seem feasible to insert a filter within the boiler at the Congress Street plant, the copper-screen type of filter was adapted, as shown in Figure 4, for insertion in the sampling line between the boiler and the cooling coil. The operation of this filter proved as satisfactory as the construction was simple. If necessary, this type of filter might readily be arranged for cleaning by back-washing.

It is believed that the fourteen layers of copper screen specified in Figure 4 will be sufficient for satisfactory filtration of any boiler water. At the Congress Street plant a filter with but six layers gave excellent results on water from the center drum, but did not completely clarify water from the

⁷ Detroit Edison Fellow in Chemical Engineering, 1930-31.

blow-off line. Another filter with twelve layers of copper screen proved satisfactory for the latter service.

The general arrangement of the sampling system relative to the boiler is shown in Detail A of Figure 5. One sampling line was taken from the water column and another from the blow-off connection on one of the mud drums. Each led to a separate copper-screen filter and cooling coil, with throttling valves on the cold discharge side of the latter. Boiler water was removed continuously through each sampling line at the rate of approximately 1 liter per minute, and was introduced at the bottom of a sampling bottle from which it overflowed into a drain trough.

An additional sampling line containing a cooling coil but no filter was connected to the blow-off line from the mud drum, as shown in Detail B of Figure 5, so that the results obtained by filtration respectively in the sampling line and in the laboratory might be compared. The complete sampling system thus made it possible to compare filtered samples obtained simultaneously from the steam drum and the mud drum, and at the same time to compare filtered and unfiltered samples from the mud drum.

FILTRATION IN SAMPLING LINE AND OF COLD SAMPLE IN LABORATORY

Three sets of samples were taken from the sampling system on the blow-off line shown in Detail B of Figure 5. In each case the sample which had not been filtered in the sampling line was filtered at once in the laboratory on a funnel in contact with the air. Total carbon dioxide was then determined on both samples by the absorption method and was calculated as carbonate, whereas hydroxide was estimated from the phenolphthalein-methyl orange titration. The results are shown in Table VI. Even with the very rapid laboratory filtration used on sample 1, there was some absorption of carbon dioxide from the air, as is evidenced by the lower hydroxide and higher carbonate for the sample filtered in the laboratory relative to the values for the sample filtered at boiler temperature in the sampling line. When slower filtration was resorted to with samples 2 and 3 in order to obtain a clear filtrate, the absorption of carbon dioxide was much more definite, the samples filtered in the laboratory showing increases of 80 and 50 per cent in carbonate as determined by the accurate absorption method. The time during which these solutions were in contact with the air of the laboratory was not more than 4 minutes.

TABLE VI. EFFECT OF FILTRATION IN LABORATORY UPON COMPOSITION OF ALKALINE BOILER WATER

SAMPLE	METHOD OF FILTRATION IN LABORATORY	SAMPLE FILTERED IN LABORATORY		SAMPLE FILTERED IN SAMPLING LINE	
		Hydroxide P. p. m.	Carbonate P. p. m.	Hydroxide P. p. m.	Carbonate P. p. m.
1	Very rapid filtration through coarse filter paper. Filtrate not clear	291	17.5	305	15
2	Filtration at maximum rate for clear sample	254	27	305	15
3	Filtration at maximum rate for clear sample	262	19	266	13

The rapid absorption of carbon dioxide by these samples of boiler water emphasizes the warning of Johnston (18) that even brief exposure to the atmosphere will lead to erroneous results. The authors believe that little attention has been paid to this point by operators responsible for boiler-water control, and that the majority of values reported for carbonate in boiler waters are high by from 50 to several hundred per cent as a result of this one factor, in addition to errors introduced by the inaccurate standard methods of titration.

No attempt was made in the present tests to determine the

possible increase in calcium in boiler-water samples as a result of filtration in the laboratory. Any error in this respect would be important only from the standpoint of fundamental research on equilibria in boiler waters and would not be significant to the operator responsible for control.

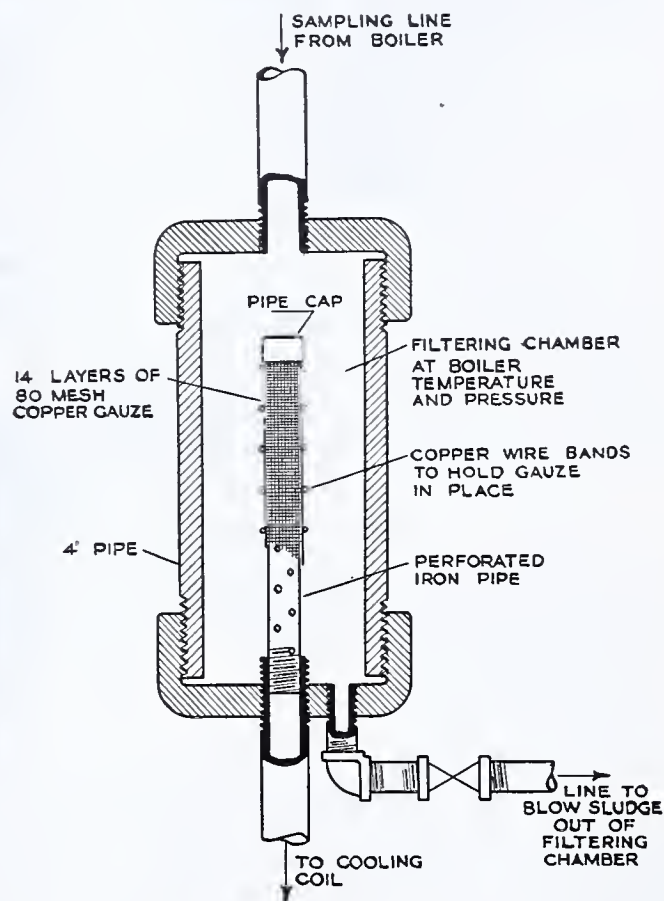


FIGURE 4. COPPER-SCREEN FILTER FOR FILTRATION OF BOILER-WATER SAMPLES AT BOILER TEMPERATURE

The tests reported establish the definite necessity for the utmost care in the handling of boiler-water samples, where carbonate concentrations must be known accurately for purposes of control. It cannot be emphasized too strongly that filtration at boiler temperature, either within the boiler or in the sampling line close to the boiler, removes one important source of error.

COMPARISON OF VALUES OBTAINED ON BOILER WATER BY DIFFERENT METHODS

Fourteen sets of boiler-water samples were taken during 3 successive days for a comparison of various methods of determining carbonate, hydroxide, and sulfate. The actual times at which samples were removed are shown in Table VII. Samples were taken simultaneously from the two lines shown in Detail A of Figure 5, all being filtered through copper-screen filters at boiler temperature before passing through the cooling coils. The pH of each sample as determined by colorimetric comparison with solution standards is given in Table VII. All samples were analyzed immediately upon removal.

CARBONATE. Values for carbonate were determined by four different methods: (1) the direct absorption method, using the simplified apparatus described in the second part of this paper; (2) the modified Winkler barium chloride titration; (3) the standard titration with phenolphthalein and methyl orange; and (4) the abridged equilibrium calculations of McKinney (30), based on the amount of acid required to titrate the sample between pH values of 8.5 and 5.0. The titration with phenolphthalein and methyl orange was made in flask D

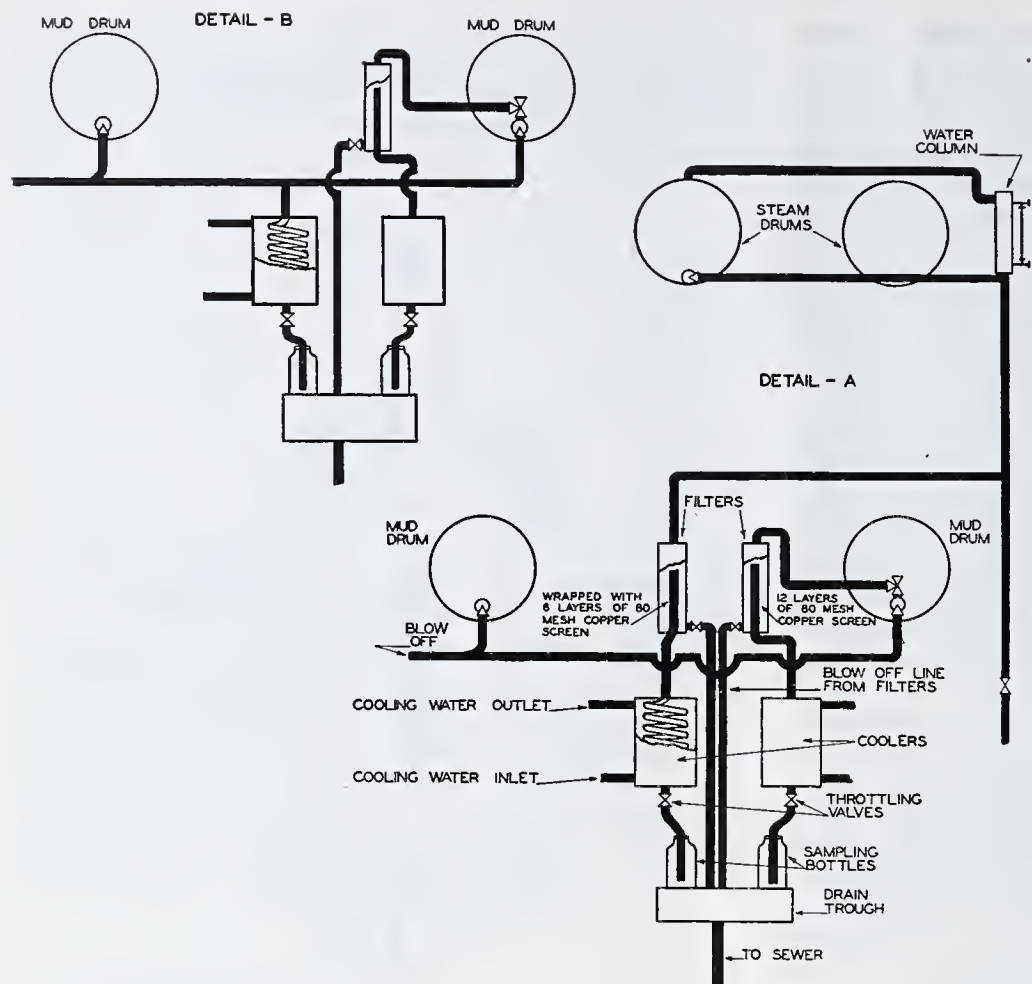


FIGURE 5. ARRANGEMENT OF SAMPLING SYSTEM FOR PLANT TESTS

of the absorption apparatus shown in Figure 3, both this determination and the absorption procedure being carried out by one of the writers. The barium chloride titration, which has been used as the control method in the Congress Street plant, was made by the regular plant operator who was not a chemist. The titration necessary for McKinney's method was made by a chemist familiar with the use of color indicators.

TABLE VII. LOG OF BOILER-WATER SAMPLES

SAMPLE	DATE	HOURL	pH ^a IN STEAM DRUM	pH ^a IN MUD DRUM
1	4-14-31	1:30 P. M.
2		2:45
3		4:00
4	4-15-31	10:00 A. M.	11.8	11.8
5		11:00	11.8	11.8
6		12:30 P. M.	11.8	11.8
7		1:30	11.8	11.8
8		2:45	11.8	11.8
9	4-16-31	4:00	11.8	11.8
10		9:30 A. M.	11.9	11.9
11		11:00	12.0	12.0
12		12:30 P. M.	12.0	12.0
13		1:30	11.9	11.9
14		2:30	11.9	11.9

^a Determined colorimetrically by comparison with La Motte solution standards.

The values for carbonate calculated from the results of the four methods of analysis are shown in Figure 6. The writers place great reliance on the accuracy of the values obtained by the absorption method which vary above and below an average value of 10 parts per million. The values indicated by all three of the other methods are high, deviating with no apparent consistency by amounts ranging from a few per cent up to 300 per cent. The results from the barium chloride titration are only slightly better than those from the titration with phenolphthalein and methyl orange. McKinney's method is subject to the same difficulties encountered with

the other titration methods when the end points at pH 8.5 and 5.0 are determined colorimetrically.

If it is granted that the accuracy of the absorption method is established by the tests on solutions of known composition reported in the second part of this paper, it is evident that none of the other methods for carbonate investigated during the plant tests was sufficiently precise for the purpose of boiler-water control.

HYDROXIDE. Values for hydroxide were calculated for the fourteen sets of samples in three ways: (1) from the phenolphthalein-methyl orange titrations; (2) from the barium chloride titrations; and (3) from the pH of the original sample using the conveniently tabulated values of McKinney (30) for the activity of hydroxyl ion at different pH values. The activity coefficients necessary to convert the activities into concentrations were estimated as 0.89 for the samples through number 9 and as 0.85 for the subsequent samples.⁸

The values for hydroxide obtained by the three methods of calculation are shown in Figure 6. It is seen that the two titration methods agree fairly well, the barium chloride method yielding values consistently somewhat lower

than those indicated by the titration with phenolphthalein and methyl orange. The hydroxide concentrations calculated from pH measurements fall still lower, with considerable deviation in the case of a few samples. Since the three concentration levels on the curve for this method in Figure 6 represent pH values of 11.8, 11.9, and 12.0, respectively, it is obvious that a slight uncertainty or error of judgment in placing the pH of samples 10, 13, and 14 at 11.9 instead of 12.0 might have been responsible for the larger deviations in the case of these samples. An error of 0.1 in the estimation of pH by comparison with colorimetric standards at intervals of 0.2 is quite possible.

Although the method of calculating hydroxide concentrations from pH proposed by McKinney for boiler-water control is theoretically sound, its rigorous application necessitates a complete analysis of the water and a determination of pH by some more accurate means than is afforded by ordinary colorimetric methods. If, as in the case of the present tests, the composition of the water is estimated from incomplete data and pH is determined colorimetrically, the values may vary in rather large jumps which will increase in size as the hydroxide concentration, and hence the pH increase. On the other hand, it was shown in the second part of this paper that both the phenolphthalein-methyl orange and the barium chloride titrations yielded satisfactory results for hydroxide with solutions of known composition. The general agreement between the two methods during the plant tests would indicate that either might be used for control purposes

⁸ Although a complete analysis of the boiler water was not made during the present tests, it was possible to estimate $\Sigma c\gamma^2$ rather closely from the determined values for carbonate, hydroxide, and sulfate by assuming concentrations of sodium, chlorine, calcium, and magnesium in line with those shown in previous complete analyses of the water. Since the feed-water is quite constant in composition, the error in determining $\Sigma c\gamma^2$ in this manner is probably less than that in the colorimetric determination of pH or the application of the Debye-Hückel equation to the calculation of the activity coefficient.

with boiler waters in which the alkalinity is due only to hydroxide and carbonate. Where phosphate or aluminate are also present, interpretation of the ordinary titrations becomes difficult if not impossible.

SULFATE. Concentrations of sulfate were determined on all fourteen sets of samples by three methods: (1) the Hagan gage (12) ordinarily used for control of the sulfate-carbonate ratio in boiler waters; (2) the old-style Parr sulfur-photometer; and (3) the benzidine titration method. In addition, sulfate was determined gravimetrically as barium sulfate on samples 10 to 14, inclusive. The results are presented in Figure 6.

The sulfate values indicated by the Hagan gage are obviously high throughout the tests relative to those obtained by the use of the sulfur-photometer and the benzidine titration. Although the last two methods are generally in fair agreement, the concentrations which they yielded were high relative to the gravimetric determinations run on samples 10 to 14.

The gravimetric method has usually been considered the most accurate means of determining sulfate concentrations. In the present case there is no reason to doubt the accuracy of the values obtained by this method, so that the burden of error must be shared to varying degrees by the other three methods. The Hagan gage is, of course, intended only for approximate estimate, although the general trend of the lines for sulfate in Figure 6 indicates that it might have given fairly consistent results if accurate calibration had been possible on the boiler water itself. The instrument was found to give correct results with sodium sulfate solutions, but the presence of other substances in the boiler water evidently affected the character of the barium sulfate suspension.

The lack of agreement between the values indicated by the Parr sulfur-photometer and the gravimetric determinations is surprising, as in previous work with an experimental boiler the turbidimetric method had generally checked very creditably the values obtained by precipitation as barium sulfate. The discrepancies in the plant results may have been due to the fact that the photometer was used in a lighted room, whereas in the laboratory it had been calibrated and used in the dark. It is also probable than an error was introduced by a different degree of dispersion of the barium sulfate precipitate in the boiler-water sample from that obtained in the pure

sodium sulfate solution used for calibration. In the tests the voltage across the lamp bulb of the photometer was maintained constant at the value previously used in the laboratory, so that no error due to variation in the intensity of the light source should have been experienced.

Better agreement with the gravimetric method than that obtained might also have been expected of the benzidine titration. The procedure followed was that outlined by Treadwell and Hall (46), except that the solution was titrated cold instead of hot. Ten minutes were allowed for precipitation and the precipitate was washed twice with 20-cc. portions of distilled water. The error was possibly due to the fact that the distilled water available in the plant contained a relatively large amount of carbon dioxide.

The actual results obtained would not justify the recommendation of any one of the rapid methods for sulfate. It is believed, however, that both the turbidimetric method and the benzidine titration may be made sufficiently exact for accurate control of boiler waters. The value of checking routine control methods against the gravimetric method is emphasized by the diverse results obtained in the present tests.

CONCENTRATIONS IN STEAM AND MUD DRUMS

The question of variation in the concentration of the water in different parts of the same boiler is frequently discussed. Throughout the present tests, during which the boiler operated at normal rating, the concentrations of simultaneous samples from the steam drum and mud drum were practically the same, as is indicated in Figure 7. In this figure the carbonate concentrations as determined by the absorption method, and the hydroxide concentrations as determined by the titration with phenolphthalein and methyl orange, are plotted for the fourteen sets of samples from the two drums. A similar plot of sulfate concentrations was not made because determinations by the accurate gravimetric method were available for but five sets of samples. The general agreement between values for the two drums by either the sulfur-photometer or the benzidine titration was, however, very good. Although some difference in concentration between the steam drums and the mud drums of a boiler may exist at high ratings because of rapid vaporization coupled with imperfect circulation, the

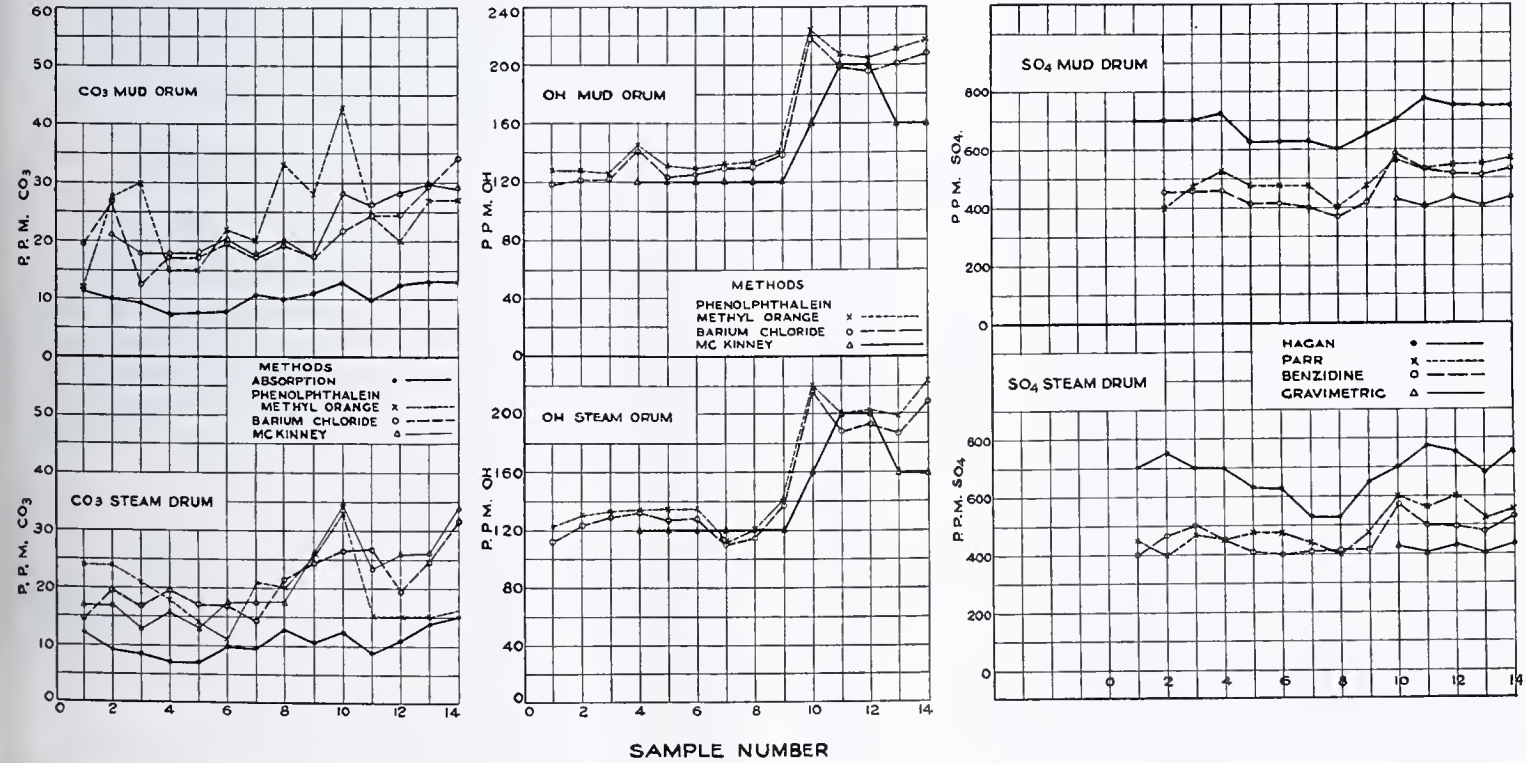


FIGURE 6. CONCENTRATIONS OF CARBONATE, HYDROXIDE, AND SULFATE IN BOILER WATER AS DETERMINED BY VARIOUS METHODS

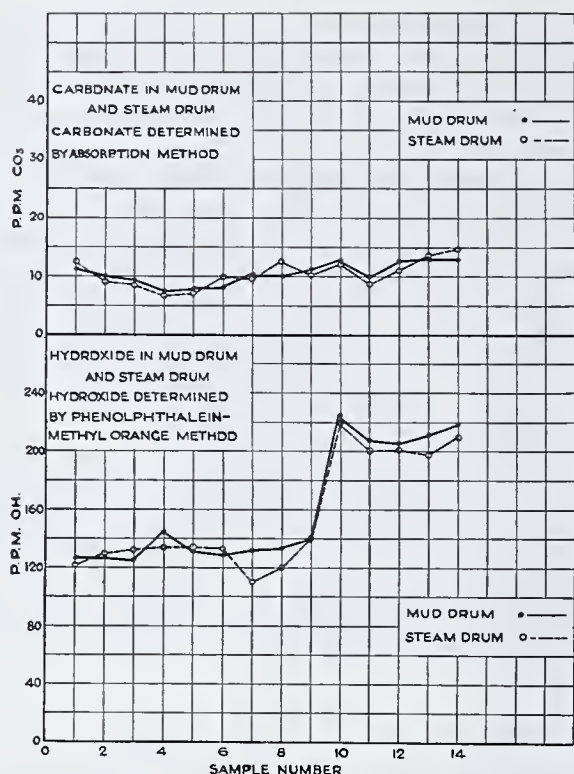


FIGURE 7. COMPARISON OF VALUES FOR CARBONATE AND HYDROXIDE IN SIMULTANEOUS SAMPLES FROM MUD DRUM AND STEAM DRUM

writers believe that such differences are smaller than they are usually conceived to be.

BOILER-CONTROL RATIOS

The rather wide variation in the results for carbonate and sulfate obtained by different analytical methods during the plant tests is significant, since it indicates that the maintenance of certain definite limits for the sulfate-carbonate ratio for scale prevention or the sodium sulfate-alkalinity ratio for inhibition of "caustic embrittlement" must have given a fictitious air of exact control in many cases where the true values were unknown and differed widely from the apparent ones. For example, at the Congress Street plant, the routine control has been based on values for sulfate obtained with the Hagan gage and values for hydroxide and carbonate calculated from the Winkler barium chloride titration. It now appears that the apparent concentrations of both sulfate and carbonate dutifully recorded for many months on the log sheets were much higher than the concentrations actually present in the boiler water. In this particular case, the apparent sodium sulfate-alkalinity ratio reported was probably always at least 50 per cent greater than the actual value, whereas the apparent sulfate-carbonate ratio reported may have been nearly correct at times and at other times very far from the actual value. This is indicated in Figure 8, where the two ratios are plotted for samples 10 to 14 as calculated both from the routine control methods and from the more accurate gravimetric method for sulfate and absorption method for carbonate.

The apparent values for the sulfate-carbonate ratio indicated by the routine control methods in Figure 8 are consistently lower than the values based on the more accurate methods of analysis, although for three of the five samples the deviation is not large, and in the other two cases the apparent values are only 25 to 30 per cent low. This relative agreement is due to the fact that the errors in both the sulfate determination by the Hagan gage and the carbonate determination by the barium chloride titration were in the same direction.

In the case of the sodium sulfate-alkalinity ratio, a large consistent error in the apparent value resulted from the high values for sulfate obtained by the routine control method. The actual values of this ratio as determined by the more accurate methods of analysis run consistently slightly under a value of 1, whereas the apparent values range from 50 to 90 per cent higher. Such a deviation might under some conditions represent the difference between safety and danger.

The inaccuracies in control methods at the Congress Street plant which were discovered as a result of the tests just reported are probably present in many other plants which pride themselves upon the exact chemical control maintained on their boiler-water conditions. The function of this paper will have been fulfilled if it stimulates other critical investigations leading to the general adoption of more accurate control methods.

CONCLUSIONS

Although the writers have no wish to discredit with one sweeping statement all of the boiler-water control analyses painstakingly recorded in hundreds of notebooks, it seems evident that any data of this type should not be accepted too seriously until the accuracy of the methods employed has been established under the actual conditions of use. The standardization of a method against pure solutions of known concentration is only the first step in proving its accuracy when applied to a complex boiler water, as is evident from the results reported in this paper.

It has been demonstrated that both the phenolphthalein-methyl orange titration and the modified Winkler barium chloride method may yield highly misleading values for carbonate in actual boiler waters. The error inherent in these methods is probably amplified in many cases by the absorption in boiler-water samples of carbon dioxide from the air. The actual carbonate concentration in any steaming boiler is probably much lower than has generally been conceded. Low carbonate concentrations in boiler waters may, however, be determined with high accuracy by the use of the simplified absorption apparatus described in this paper.

In view of the probable low limit of carbonate concentration in an operating boiler, discussion as to whether sodium carbonate should or should not be taken into account as an inhibiting agent in the calculation of the embrittlement ratio is almost pointless. It appears, however, that the prescribed ratio values may be equally pointless, owing to possible large errors in routine control determinations of sulfate. An investigation of this matter should be made.

The routine determination of hydroxide concentrations in boiler waters is probably subject to less error than the deter-

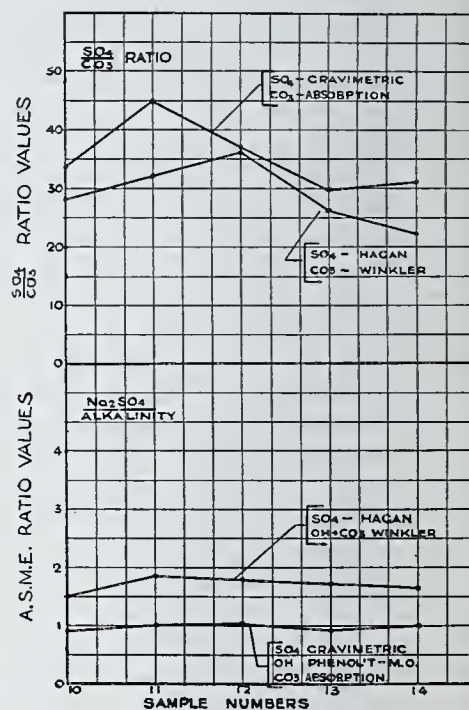


FIGURE 8. COMPARISON OF VALUES OBTAINED BY VARIOUS METHODS FOR SULFATE-CARBONATE SCALE-PREVENTION RATIO AND FOR SODIUM SULFATE-ALKALINITY RATIO FOR INHIBITION OF EMBRITTLEMENT

minations of either carbonate or sulfate since, when limited to its purpose of measuring the hydroxide concentration, the original Winkler barium chloride method yields satisfactory results. The value for hydroxide indicated by the phenolphthalein-methyl orange titration should also generally not be far in error unless unusual amounts of phosphate, aluminate, silicate, or similar ions of slightly dissociated acids are present.

ACKNOWLEDGMENT

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Removal of Color from Solutions to Be Examined by Color Comparisons

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FOR determination of phosphate in soil extracts by the molybdenum blue method and for some other purposes a colorless solution is desired. The color may be removed from most such solutions by the following simple procedure.

To 50 cc. of the colored solution add 5 cc. of saturated solution of bromine water and 5 drops, or enough to make alkaline, of 5 N sodium hydroxide. Mix, the brown color should disappear, showing that the solution has become alkaline. Add 5 drops of 5 N hydrochloric acid, or other suitable acid, to make the solution acid again. Free bromine should now be apparent; if not, the treatment should be repeated from the first. Now add a little (5 cc. of a 5 per cent solution) sodium sulfite to reduce the bromine and leave the solution colorless. The bleaching action seems to take place mostly at the moment the bromine is liberated by adding acid to the sodium hypobromite first formed. In the alkaline

state, the color is slowly removed but, when acidified, the solution becomes colorless instantly in the presence of sulfur dioxide.

If there is any objection to the use of sodium sulfite for removing the free bromine, it may be expelled by boiling or by passing air through the solution for a time. Excess of sodium sulfite is not objectionable in the solution in which phosphate is to be estimated by the molybdenum blue method.

The procedure described removes the color from soil extracts, plant extracts, dye solutions, indicator solutions, etc. If the solution is strongly colored, it may be necessary to use more than 5 cc. of bromine water. Of course, the bromine water and the sodium hydroxide may be combined and used as a single solution, although it appears that the bleaching power of the sodium hypobromite is gradually lost with time.

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Rapid Determination of Zinc and Other Impurities in Cadmium

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THE usual methods for the determination of impurities in cadmium depend upon the preliminary separation of the cadmium as sulfide and the subsequent estimation of the other elements sought. This procedure is not entirely satisfactory when the metal is relatively pure. Since the pH ranges through which cadmium, lead, and zinc may be precipitated as sulfides are quite close together, it is difficult to separate them when the cadmium is preponderant. It is then necessary to pass large samples through a laborious series of filtrations and evaporations in order to separate the impurities. Consequently, the analysis is tedious and expensive. In view of this, a rapid, routine method of analysis would be very acceptable.

Numerous methods have been published for the determination, with a minimum of separations, of impurities in most of the common metals. Some of these methods, it was believed, could be adapted to the estimation of lead, copper, zinc, iron, arsenic, and sulfur in cadmium metal. These procedures were studied to determine what modifications, if any, were necessary in order to secure concordant results in the presence of large amounts of cadmium.

Well-known methods for lead, copper, iron, arsenic, and sulfur were found to be easily applied to this determination. The estimation of zinc, however, offered more difficulties.

A survey of the literature dealing with the detection and estimation of small quantities of zinc disclosed that a number of precipitation methods have been proposed. Unfortunately cadmium seemed to interfere seriously in all such procedures. A preliminary examination indicated that the qualitative method proposed by Montequi (12) would probably be more adaptable to the determination of zinc in cadmium than any other method.

Behrens and Burgeois (6) state that the reaction of the salts of copper with mercuric ammonium thiocyanate is greatly modified in the presence of zinc salts. If the copper is present in considerable excess, irregular granules of a blackish color are produced. However, when the zinc salts predominate, the precipitate formed is crystalline and of the characteristic zinc form, but has a chocolate color. This reaction was examined by Montequi (12) who concluded that, when the mercuric ammonium thiocyanate is added to a mixture of copper and zinc salts, the latter in excess, the zinc salt has the property of forming mixed crystals with a black mercuric cupric thiocyanate. To this body is due the intense violet color of the precipitate. The composition of the crystals was found to correspond to the formula, $\text{CuZn}[\text{Hg}(\text{SCN})_4]_2$. These mixed crystals were found to be isomorphic with $\text{ZnHg}(\text{SCN})_4$. Cadmium likewise forms a violet precipitate under the same conditions, but not quite as readily as zinc.

Montequi proposed a qualitative method for the detection of as small quantities of zinc as 0.00005 gram in 2 or 3 ml. of solution. It consists essentially in the addition, to a neutral solution, of a very small amount of copper, followed by mercuric ammonium thiocyanate. After thorough mixing, an intensely violet precipitate indicates zinc. Hammond (9) adapted this method to the estimation of small quantities of zinc in storage battery electrolyte.

DEVELOPMENT OF METHOD

The most serious difficulties in the adaptation of this reaction to the estimation of zinc in cadmium rested in the precipitation of the cadmium itself and in the tendency of the cadmium solution to prevent the precipitation of the zinc compound.

The effect of concentration on the reaction was determined by treating a series of cadmium solutions with the reagents recommended by Montequi. The results showed that cadmium precipitates readily from dilute solutions (1 per cent) but more slowly as the concentration increases. At a concentration of 0.85 gram of cadmium chloride per ml., the precipitate formed is slight, even after standing overnight. The results when using other salts were not so satisfactory as with the chlorides. Free mineral acids were found to be the cause of very erratic behavior, but the addition of sodium acetate neutralizes the free acid so that reproducible results may be obtained.

To a series of solutions containing 0.5 gram of cadmium per ml. were added increasing amounts of zinc, followed by the precipitation reagents. It was found that the precipitates produced in the cadmium solutions were distinctly less in amount than in pure water solutions of equal zinc concentration. According to the statement of Behrens (5) which Montequi questions, the presence of cadmium salts interferes somewhat with the precipitation of the zinc salt. It is evident that the view of Behrens is correct, but this interference is not sufficient to prevent the formation of the zinc precipitate entirely, although it does reduce the sensitivity of the reaction from 0.00005 gram in 2 or 3 ml. to 0.0001 gram in 5 ml.

In order to use this reaction as a measure of the amount of zinc present in cadmium, it was necessary to show that regularly increasing amounts of zinc produced corresponding changes in the appearance of the precipitate formed. This was done by using zinc-free cadmium chloride, adding known amounts of zinc, and then treating with the precipitation reagents. The results were gratifying, as 5 ml. of solution containing 2.5 grams of cadmium as cadmium chloride and no zinc gave a slight, pale flesh-colored precipitate after standing 15 minutes. Other 5-ml. portions containing increasing quantities of zinc in increments of 0.0002 gram of zinc produced precipitates whose color and abundance increased regularly with the zinc concentration. Smaller increments of zinc had the same effect, but the change from one increment to the next was too small to be of value as a quantitative measure. The precipitates were allowed to stand overnight, when it was found that the intensity of color had increased noticeably. The differences in appearance were much more distinct than after the first 30 minutes. No further changes were apparent after standing 3 days.

At this point it should be noted that, under the conditions outlined below, the intensity of color increases regularly with the zinc concentration. When the reaction is carried out in dilute solutions, the color is most intense when the zinc concentration is smallest (12) although the abundance of the precipitate varies directly with the amount of zinc present.

The question of interference of other probable impurities in cadmium metal was then taken up. Copper was found to

¹ Address at P. O. Box 1121, Vallejo, Calif.

increase the intensity of color of the precipitate, but to have no appreciable effect upon the amount of precipitate. If, however, there is more copper present than zinc, a green precipitate, CuHg(SCN)_4 (12), is formed in addition to the usual violet. Iron in small quantities gives a reddish color to the solution and changes the color of the precipitate slightly by occlusion. Lead, manganese, aluminum, and chromium do not interfere.

SCHEME OF ANALYSIS

ZINC

REAGENTS. Blank solution, 97.46 grams of $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$ dissolved in sufficient water to make 100 ml.

Copper sulfate, 0.2 gram of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 1 drop of sulfuric acid dissolved in 100 ml. of water.

Mercuric ammonium thiocyanate. Grind 8.0 grams of mercuric chloride and 9.0 grams of ammonium thiocyanate in a mortar with a small amount of water. Add water to make 100 ml., and then filter.

Zinc standard, 2.1 grams of zinc chloride dissolved in 100 ml. of water.

Sodium acetate, saturated solution in water.

METHOD. Place 12.5 grams of the finely divided sample in a 150-ml. beaker, on a piece of platinum foil. Cover with a watch glass and add 25 ml. of concentrated hydrochloric acid. Warm until nearly all the cadmium is in solution, adding more acid as necessary. Decant the solution, wash the residue, foil, and cover with a minimum of water. Discard the residue. Evaporate the solution to dryness and bake until the odor of hydrochloric acid is gone. Add 15 ml. of water, agitate, and warm until solution is complete. Cool, transfer to a 25-ml. flask, and fill to the mark.

Transfer 5.0 ml. of this solution to a small, narrow beaker or test tube. Add 1 drop of sodium acetate solution to neutralize the remaining acid. Mix thoroughly, then add 1 drop of copper sulfate solution, mix again, and finally add 0.5 ml. of mercuric ammonium thiocyanate solution. Mix thoroughly and allow to stand at least 30 minutes.

Prepare a series of standards by adding zinc solution in increments of 0.02 ml. of zinc standard to 5.0-ml. portions of the blank solution. Add 1 drop of sodium acetate solution and proceed exactly as with the sample. Match the precipitate formed in the unknown with the standards, both as to color and abundance. The precipitate settles quickly and may be gathered into the center of the beaker by swirling the liquid with a rotary motion of the arm.

Iron and copper would interfere if present, but the method of solution eliminates the copper and most of the iron. The small amount of iron that goes into solution does not influence the precipitation appreciably. Lead, manganese, aluminum, and chromium do not interfere. Free mineral acids should be absent.

The method is effective between 0.0001 and 0.003 gram of zinc in 5 ml. of solution. It is essential that the reagents be as concentrated as practicable so that their addition will not cause excessive dilution. The use of a more concentrated copper solution causes the precipitate to form more quickly, but the differences in the standard series are less distinct.

LEAD

Lead is determined by the A. S. T. M. electrolysis method (2). Dissolve 20 grams of the metal in 40 ml. of concentrated nitric acid. Boil to remove oxides of nitrogen. Dilute to 125 ml., and electrolyze with a current of 5 amperes for 45 minutes. Lead will deposit on the anode as lead oxide. Wash lightly, dip in alcohol, dry, and weigh.

$$\text{PbO}_2 \times 0.864 = \text{Pb}$$

Cadmium, iron, copper, etc., do not interfere.

COPPER

This method is based upon the xanthate method as described by Scott (14).

REAGENTS. Potassium ethyl xanthate, 0.1 per cent in water, freshly prepared.

Copper standard, 0.039 gram of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dissolved in 100 ml. of water.

Sulfuric acid, 5 per cent.

METHOD. Prepare a stock solution for the determination of copper and iron. Dissolve 5 grams of sample in 20 ml. of concentrated nitric acid. When solution is complete, add 20 ml. of sulfuric acid (1 to 1) and heat carefully until copious fumes of sulfur trioxide are evolved. Cool, add 35 ml. of water, and agitate until solution is complete, warming if necessary. Cool, transfer to a 50-ml. flask, and add water to make 50 ml.

Transfer 25 ml. of the stock solution to a 150-ml. beaker, add 40 ml. of water and 10 ml. of xanthate reagent. Mix thoroughly. Prepare a standard by adding 10 ml. of the reagent to 65 ml. of 5 per cent sulfuric acid. Then add copper standard in 1-ml. portions until the brown tints match.

Nitrates interfere with the development of the color. Other probable metals do not interfere.

IRON

Iron is determined by the method of Lyons (11).

REAGENTS. Thioglycollic acid.

Standard iron solution, 0.007 gram of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ dissolved in 100 ml. of water.

METHOD. Place 1 ml. of the stock solution prepared for copper in a small beaker or comparison tube. This represents a 0.1-gram sample. Add 10 ml. of water and 5 ml. of concentrated ammonium hydroxide. Mix, and then add 0.5 ml. of thioglycollic acid and mix thoroughly. A red or purple color shows iron. Compare this color with that produced by the standard iron solution in varying amounts in the same total volume.

Cadmium interferes unless a decided excess of ammonia is present. Oxidizing agents also interfere.

ARSENIC

Details of the construction and manipulation of the Gutzeit apparatus may be obtained from Scott (13).

REAGENTS. Mercuric chloride strips, small (12).

Hydrochloric acid, arsenic-free (1 to 1).

METHOD. Place a 10-gram sample on a piece of platinum foil in the bottom of the apparatus. Add 50 ml. of hydrochloric acid (1 to 1, arsenic-free) and close the apparatus. Omit the usual addition of zinc, since it interferes with the solution of the cadmium. Warm on a hot plate until action ceases. Do not boil. Compare the resulting stain on the mercuric chloride strip with the standard stains.

None of the probable impurities interferes.

SULFUR

An evolution method, substantially the same as that recommended by Scott (15), is used.

REAGENTS. Iodine solution, 0.02 N.

Cadmium chloride solution, 20 grams of $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in water. Add ammonium hydroxide until the precipitate redissolves. Acidify with acetic acid, and add 20 ml. excess. Make up to 1000 ml. with water.

METHOD. Place 5 grams of the finely divided sample in the evolution flask on a piece of platinum foil. Then assemble the apparatus with the gas outlet in an absorption flask containing cadmium chloride solution. Add 50 ml. of hot water

to the evolution flask, followed by 50 ml. of concentrated hydrochloric acid. Warm gently until solution is complete, and then introduce carbon dioxide into the evolution flask, either as carbonate solution or as gas, to flush out the apparatus. Acidify the contents of the absorption flask with hydrochloric acid and titrate with iodine solution in the usual manner.

None of the usual impurities interferes.

ACCURACY OF RESULTS

The results on four samples by the above procedure were compared with those obtained by the following methods:

Copper was deposited from a 50-gram sample in nitric acid solution by electrolysis. The copper was redissolved and redeposited (7).

Iron, A. S. T. M. method B-38-21 using 25-gram sample (4).

Lead, A. S. T. M. method B-38-21 using 50-gram sample (3).

Arsenic. The Gutzeit method for arsenic in small amounts is considered standard. Hence the accuracy of this use of the method was not investigated.

Sulfur was determined by the oxidation method of the A. S. T. M. (1), except that the nitric acid used for dissolving the metal was saturated with bromine. Twenty grams of sample were used.

Zinc. The method of the Committee on Analytical Reagents of the AMERICAN CHEMICAL SOCIETY (8) was altered to accommodate larger samples as follows: A 25-gram sample was dissolved in hydrochloric acid with the aid of a platinum catalyst. The solution was evaporated to dryness and the excess acid driven off. The residue was then dissolved in hot water, and sulfuric acid was added at the rate of 3.5 ml. per 100 ml. of solution. Hydrogen sulfide was then passed into the solution until no further precipitation took place. The cadmium sulfide was filtered off, the filtrate was evaporated to dryness, and the excess acid again driven off. This process was repeated until no further precipitate was obtained in the solution containing 3.5 ml. of sulfuric acid per 100 ml. of solution.

The cadmium sulfide was reprecipitated to remove occluded zinc. The final solutions were combined and evaporated until nearly all the excess sulfuric acid had been driven off. The residue was dissolved in water, neutralized with sodium

hydroxide, and then acidified with 0.1 *N* sulfuric acid. The zinc was then removed as zinc sulfide, dissolved in hydrochloric acid, and precipitated with sodium acid phosphate. This precipitate was ignited and weighed as $\text{Zn}_2\text{P}_2\text{O}_7$ (10).

The following table gives a comparison of the results obtained:

SAMPLE	METHOD	ARSENIC %	SULFUR %	COPPER %	IRON %	LEAD %	ZINC %
1	A ^a	0.0001+	None	0.010	0.012	0.001	0.004
	B ^b ^c	None	0.013	0.009	None	None
2	A	0.001	None	0.004	0.004	0.006	0.028
	B	None	0.011	0.007	0.002	0.025
3	A	0.0001	0.014	0.004	0.008	0.055	0.016
	B	0.006	0.003	0.007	0.059	0.019
4	A	0.0001	0.010	0.032	0.020	0.028	0.008
	B	0.004	0.036	0.016	0.030	0.010

^a Proposed method.

^b Other method as outlined.

^c Arsenic determined by Gutzeit method only.

It will be noted that the proposed procedure requires no filtrations and but one separation in the entire scheme of analysis. This is in marked contrast to the many filtrations necessary when other methods are used.

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Determination of Relative Humidities by Means of Thermocouples

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FOR certain types of work it is necessary to have a definite relative humidity in a small space such as a desiccator. Mixtures of sulfuric acid and water are usually relied upon as a means of control, but if the substance under test is constantly giving off unknown quantities of moisture, then the actual relative humidity is always somewhat in doubt. For a particular piece of work this difficulty was encountered, so it was necessary to devise a means for roughly checking the relative humidity. Wet- and dry-bulb thermometers were impractical, since the amount of moisture evaporated from the wet bulb would be sufficient to change the equilibrium between the acid solution and the air.

It was found that relative-humidity determinations can be made by means of two small thermocouples, one of which has a small drop of water surrounding it. Because of the evapora-

tion of water from this drop, a difference in temperature is produced which causes the couples to exhibit a definite potential difference, which may be measured by a sensitive instrument such as a Leeds and Northrup type K potentiometer in combination with a sensitive galvanometer. This voltage difference, when calculated to degress Fahrenheit, is not the same as the temperature difference shown by wet- and dry-bulb thermometers, but is always lower. This is probably due to the difference in transfer of heat of metals and glass, and could possibly be further minimized by the use of smaller couples than those which will be described. However, it was found that the relation between the two was practically a straight-line function, so it was a fairly simple matter to construct the curve illustrated in Figure 1 showing the relationship between millivolt differences and wet- and

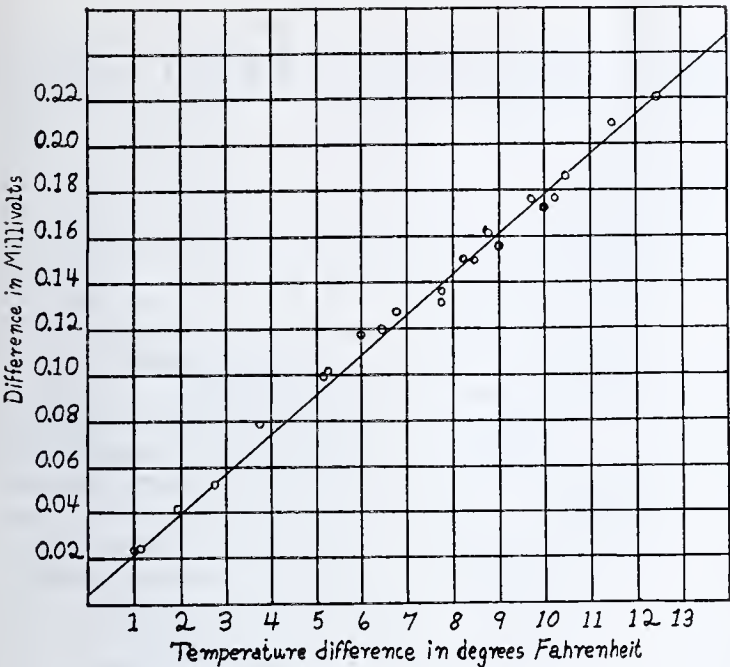


FIGURE 1. MILLIVOLT DIFFERENCES VS. WET- AND DRY-BULB TEMPERATURE DIFFERENCES

dry-bulb temperature differences at definite relative humidities.

The thermocouples are made by fusing a copper wire about 60 cm. in length to each end of a 15-cm. piece of constantan wire. These wires should be 0.02546 cm. in diameter (No. 30 B. & S. gage). This fusion is readily accomplished by holding the two wires in the flame of a Bunsen burner until the ends begin to melt, when they are brought together and fused into a small bead. The copper wires may then be covered with an insulating material and used as electrical leads.

At one of the thermocouples four small loops are made by winding the wire four times around a nail with two turns on each side of the point of fusion. When the nail is withdrawn, a small coil will remain which should be 2 or 3 mm. in diameter and which serves to hold a drop of water which will remain suspended owing to its surface tension.

TABLE I. CONVERSION OF RELATIVE HUMIDITIES TO EQUIVALENTS OF WET- AND DRY-BULB TEMPERATURE DIFFERENCES

DIFFERENCE	RELATIVE HUMIDITY		ROOM TEMP.
	OBTAINED WITH ACID SOLNS.	EQUIV. IN WET- AND DRY-BULB DIFF.	
<i>Millivolts</i>			<i>° F.</i>
0.023	96	1.0	75
0.024	94	1.2	67
0.041	91	2.0	75
0.052	86	2.8	65
0.078	83	3.8	73
0.101	77	5.3	76
0.089	76	5.2	70
0.117	74	6.0	74
0.127	70	6.8	72
0.119	69	6.5	67
0.131	65	7.8	70
0.150	64	8.3	72
0.155	61	9.0	72
0.149	61	8.5	69
0.136	61	7.8	64
0.161	60	8.8	69
0.176	59	9.8	74
0.176	58	10.3	76
0.172	57	10.0	72
0.186	56	10.5	74
0.209	51	11.5	73
0.220	48	12.5	73

The drop may be supplied automatically by suspending a small glass tube of water above the coil in such a manner that the water will feed into it as required. This tube must be drawn to a capillary at one end and partially sealed at the other. It is suspended so that the capillary end is immersed in the drop and is set at such an angle that some of the water

flows out. Equilibrium is soon reached and water flows from the capillary end in the amount necessary to replenish the drop.

In order to obtain the value of the voltage readings in terms of relative humidity, the following procedure was used: The thermocouples were placed in a large desiccator with a side opening and the leads brought out through this opening. A one-hole rubber stopper was inserted to separate them, and a piece of glass tubing was run through the hole to serve as a bearing for the shaft of a small fan which served to keep the air circulating around the wet couple. The fan shaft was given a thick coating of vaseline which served as a lubricant and also to make the apparatus more nearly air-tight. A cork was used as a pulley and a small electric motor furnished the driving power. The essential apparatus is illustrated in Figure 2.

The humidity within the desiccator was controlled by means of solutions of sulfuric acid and water. Approximate amounts of acid were added to the water and the specific gravity taken. From this the exact percentage of acid in the mixture and the humidity produced was ascertained by reference to tables (2). Both the solution and the air under observation were kept at as nearly the same temperature as possible.

The feed tube was filled with water and mounted so that it would feed the drop which was suspended in the coiled couple. The lid was then replaced and the fan started. The apparatus was allowed to remain undisturbed for a period of at least 30 minutes, when the voltage differences developed by the couples were determined with the type K potentiometer. After another 5 or 10 minutes, another reading was taken to make certain that

equilibrium had been reached. This procedure was carried out for a number of different values of relative humidity and the results are given in Table I. The temperatures at which the determinations were made were observed with a mercury thermometer.

The relative humidities indicated by the acid mixtures were converted to their equivalents of wet- and dry-bulb temperature differences from Table VI of Marvin's Psychrometric Tables (1), and these results are also shown in Table I. The wet- and dry-bulb temperature differences were plotted against the differences in millivolts obtained between the thermocouples, and are graphically shown in Figure 1. A working curve is thus obtained from which millivolt differences can be converted to wet- and dry-bulb temperature differences. These temperature differences can then be directly converted into relative humidity figures from psychrometric tables.

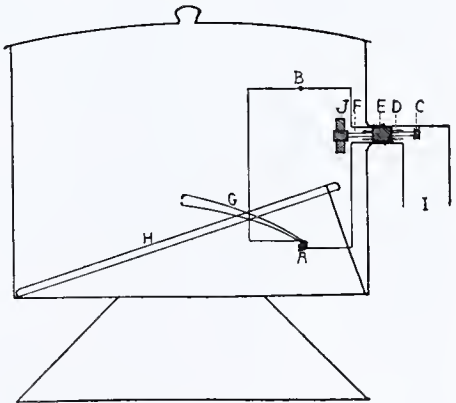


FIGURE 2. APPARATUS FOR VOLTAGE READINGS

- A. Wet thermocouple
- B. Dry thermocouple
- C. Pulley
- D. Bearing
- E. Rubber stopper
- F. Fan shaft
- G. Water-supply tube
- H. Support for water-supply tube
- I. Electrical leads to potentiometer
- J. Fan

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Occurrence and Determination of Iron in Sea Water

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IRON has frequently been detected in sea water, but very few attempts have been made to determine it quantitatively (4, 5, 7, 16, 17, 18). In many of the references to the subject, neither the method of detection nor the amount of iron found is mentioned, and no systematic study seems to have been made to show the distribution of iron with depth. Sea water does not contain ferrous or ferric ions, and all available evidence points to the conclusion that the iron exists in the form of soluble organic compounds. In every instance where the method of detection of the element is described, the sample of water was first subjected to some form of oxidation in order to decompose the organic matter. Using nitric acid, Harvey (4) obtained from 0.003 to 0.006 mg. of iron per liter; Wattenberg (18) reported 0.06 mg.; Orton (7), using bromine water, obtained 0.1 mg.; and Vernadsky (17) gave a result of 1.5 mg. Recently Braarud and Klem (1) have reported results on the Norwegian fjords varying from 0.004 to 0.023 mg.

Although bromine water and nitric acid doubtless oxidize much of the organic matter, organic acids might be formed as a result of this oxidation that would retard the usual tests for iron in much the same manner as tartrates and oxalates. Furthermore, Gautier and Clausman (2) have shown that sea water contains as much as 0.3 mg. of fluorine per liter, and it is logical to conclude that the presence of fluorides would favor the formation of the stable ferrifluoride ions, and thus hinder the usual colorimetric reactions employed in the detection of minute quantities of iron.

NATURE OF THIOCYANATE REACTION

Various reagents have been recommended for the estimation of traces of iron. After preliminary studies, the authors decided upon the use of the thiocyanate reagent because of its reliability in yielding readily reproducible results. The color produced by the thiocyanate and ferric ions has been known since 1837 (8) and has been the subject of considerable study. Recently Schlesinger and Van Velkenburgh (9) have shown by means of absorption spectra of aqueous and ethereal solutions and the electrolysis of aqueous solutions that the red color is due to the complex ion $[\text{Fe}(\text{CNS})_6]^{---}$.

Different authorities have shown that organic compounds, iodic and hydrosulfuric acids, chlorides of the alkaline earths, nitrates, nitrites, fluorides, phosphates, arsenates, and sulfates, all of which occur in sea water, prevent or considerably retard the formation of the color. However, the phosphates and arsenates are present in such small quantities that they need not be considered, if the conclusions of Leeper (6) are accepted. The chlorides of the alkaline earths occur in

Sea water contains many substances which interfere with the usual colorimetric thiocyanate method for the determination of iron. A method has been devised for the analysis of iron in sea water by removing these with sulfuric acid.

The effects of sulfates and sulfuric acid upon the thiocyanate reaction due to the formation of complex ferrisulfate ions may be controlled by the use of equivalent quantities of sulfates and sulfuric acid in the standards by utilizing a large excess of the thiocyanate reagent, and by causing the reactions in the samples and standards to take place at a constant temperature.

Surface sea water shows a seasonal variation in the iron content, which is evidently diminished at times of maximum diatom growth. Iron content generally increases with depth.

quantities sufficient to affect the results materially.

Wide variations in the concentrations of sulfates have a decided effect, but the authors have found that by maintaining approximately the same sulfate concentration in the samples as well as in the standards used for comparison, very good results, which were easily reproducible, could be obtained. Thus by treating the samples with sulfuric acid and evaporating to sulfuric fumes, all the chlorides, nitrates, nitrites, fluorides, and much of the organic matter would be removed.

The interference of the sulfate ions is due to the formation of a complex ion, probably represented as $[\text{Fe}(\text{SO}_4)_2]^-$ (10).

This is not as stable as the ferrithiocyanate complex, and therefore, by applying the law of mass action, the addition of a large excess of thiocyanate reagent greatly favors the formation of the colored compound.

DETERMINATION OF IRON

REAGENTS. The sulfuric acid used must be 36 N and iron-free.

For potassium permanganate, 6.30 grams are dissolved in water to give a solution of 1 liter. The reagent should be tested to insure the absence of iron.

To obtain bromine water a bottle of distilled water is saturated with iron-free bromine. The reagent has been found to react with the iron contained in the glass of the reagent bottle. Use of bromine water that has been stored for some time should thus be avoided.

For potassium thiocyanate, 480 grams are dissolved in water to make a stock solution of 4 liters.

For sodium sulfate, 1800 grams of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ are dissolved to make approximately 4 liters. This is equivalent to a saturated solution of the salt at 20° C. To this solution 1.5 ml. of a concentrated solution of sodium hydroxide are added and, after heating and stirring thoroughly, the solution is filtered to remove any traces of iron that may have precipitated. The filtrate is then treated with a sufficient quantity of standard sulfuric acid to just neutralize the excess of alkali. Portions of this solution are used in the preparation of standards.

To make standard iron solution 0.70 gram of ferrous ammonium sulfate is dissolved in 50 ml. of water, 20 ml. of 6 N sulfuric acid are added, and permanganate reagent introduced into the hot solution until the color persists for 5 minutes. A drop of bromine water is added to decolorize the solution which, after transferring to a volumetric flask, is made up to a volume of 1 liter containing the equivalent of 0.1 mg. of iron per ml. Before using this solution it is again diluted so that 1 ml. is equivalent to 0.01 mg. of iron.

Iron wire may be used in lieu of the ferrous ammonium sulfate.

PROCEDURE. A 100-ml. sample of the sea water is measured into a 500-ml. Erlenmeyer flask, 6 ml. of 36 *N* sulfuric acid added, and the solution evaporated to sulfuric fumes to remove the chlorides, fluorides, nitrates, nitrites, and bring about the destruction of much of the organic matter. While the solution is still warm, 85 ml. of water are carefully added and the flask, covered with a watch glass, is heated on the steam bath until the alkaline earth sulfates have dissolved. Potassium permanganate is then added, drop by drop, to the hot solution until the color persists; two drops have been found to be sufficient in most cases. The excess permanganate is decolorized by adding 1 ml. of bromine water. After boiling off the excess bromine, the solution should be perfectly clear with no sediment except possibly a trace of white siliceous material. The clear solution is then permitted to cool, placed in a 100-ml. Nessler tube, and treated in the same manner and at the same time as the iron standards with 10 ml. of thiocyanate reagent.

PREPARATION OF IRON STANDARDS

The standard iron solution is measured from a microburet into a series of 500-ml. Erlenmeyer flasks, each of which contains 22 ml. of the sodium sulfate reagent, 50 ml. of water, and 5 ml. of 36 *N* sulfuric acid. Since the usual range of iron content is 0.00 to 0.20 mg. of iron per liter and 100-ml. samples are used, the standards should contain 0.00, 0.001, 0.003, 0.005, 0.007, 0.010, 0.015, and 0.020 mg. of iron. The standards are treated with permanganate solution and bromine water as described above, and finally transferred to 100-ml. Nessler tubes. Ten millimeters of thiocyanate reagent are added to each tube. It is very important that these standards be treated with the thiocyanate at the same time as the regular samples.

The color produced by the thiocyanate fades, but in the above dilutions fading is not very rapid, especially if comparisons are made in well-diffused light. About 20 samples can be run conveniently with each set of iron standards. It has been found advisable to have the equal portions of thiocyanate reagent already measured either in a series of small graduates or in test tubes, so that the time required for adding the reagent to all the samples and standards shall be as small as possible.

The quantity of sodium sulfate used in the standards has been calculated as equivalent to the major cations of a sea water of chlorinity of 18.7 per liter at 20° C. (3, 10, 11, 13, 15, 17). Such a quantity of sulfate, together with that added as sulfuric acid, exerts a very marked effect upon the color obtained, imparting a more brownish tint and decreasing the intensity considerably below that of standards without the presence of sulfates. The color is more stable at lower than at higher temperatures. It is imperative that all of the samples and standards be at the same temperature before treating with the thiocyanate reagent.

PRECAUTIONS. Well-seasoned bottles should be used for samples of sea water to eliminate the possibility of contamination due to the leaching of iron from the glass container. It is essential that fresh samples of water be used for analysis, as the growth of diatoms will remove most of the iron from solution if the samples are permitted to stand. Waters rich in plankton should be filtered immediately upon sampling. Should it be impossible to analyze the samples for some time, they should be acidified with sulfuric acid before storing.

EFFECT OF DIATOMS UPON IRON CONTENT OF SEA WATER

In the summer of 1931, samples of sea water were collected in an estuary of the San Juan Archipelago (East Sound), from

four different depths at each of three stations. The samples were exceedingly rich in diatoms and were permitted to stand in the laboratory for a period of 2 months. At the end of that time, samples of the filtered and unfiltered sea water were analyzed with the average results for the three stations as shown in Table I. Owing to the large amount of suspended material in the unfiltered samples resulting from the growth of diatoms, several modifications of the method were necessary in

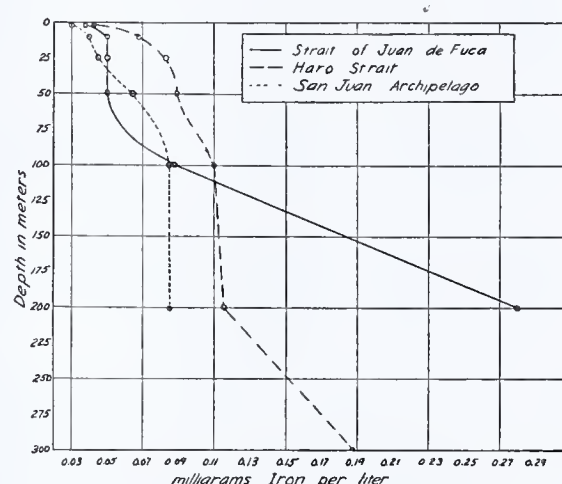


FIGURE 1. VARIATION OF TOTAL IRON CONTENT

order to insure complete destruction of the organic matter. At the time of sampling, the average iron content of the water of the San Juan Archipelago was 0.03 to 0.04 mg. per liter. The data given illustrate the effect produced by permitting samples to stand and the necessity of preventing growth of the diatoms.

TABLE I. IRON CONTENT OF WATERS RICH IN PHYTOPLANKTON
(Samples stood several months before analysis)

DEPTH Meters	FILTERED SAMPLES Mg. Fe/liter	UNFILTERED SAMPLES Mg. Fe/liter
1	0.00	0.04
5	0.00	0.03
10	0.00	0.05
20	0.01	0.07

IRON CONTENT OF WATERS OF SAN JUAN ARCHIPELAGO AND STRAIT OF JUAN DE FUCA

SEASONAL VARIATION. Surface samples were collected once a week for a period of 1 year beginning September, 1928, at Friday Harbor, Washington. From these weekly samples, monthly composite samples were prepared. The highest results, 0.05 mg. and 0.06 mg. of iron per liter, were obtained in March and April, but these were followed by a decrease through May to July when the lowest result, 0.032 mg. of iron per liter, was noted. A slight decrease in the iron content was likewise observed in December and February. The average for the year was 0.042 mg. of iron per liter. Because of certain imperfections in technic at the time these determinations were made, the authors believe the results to be low; it is the relative variation that is of particular interest.

The waters of Puget Sound are remarkably high in the so-called nutritive material, such as phosphates, nitrates, etc. (12, 14). This is caused by the up-welling of the deeper ocean waters, rich in nutritive salts, off the continental shelf, and also is largely due to the strong tidal-current effect in the deep, canyon-like shape of the ocean floor at the entrance to the Strait of Juan de Fuca. In the spring and summer months the waters are characterized by a rich growth of diatoms in the surface layers down to depths of approximately 25 meters.

In the summer of 1931, cruises in the San Juan Archipelago, Haro Strait, and the length of the Strait of Juan de Fuca to the Pacific were made. Table II gives a summary of the iron

content in the waters of the several stations. The chlorinities of the waters of the Strait of Juan de Fuca are greater than those of Haro Strait, and those of Haro Strait are greater than those of the San Juan Archipelago. The data represent the average of four stations in each body of water. The stations in Haro Strait were taken to the westward of San Juan Island. These stations are characterized by their greater depth and the exceedingly marked turbulence of the waters produced by the strong tidal currents striking the almost perpendicular submarine cliffs off the shore of the island.

TABLE II. IRON CONTENT OF WATERS OF STRAIT OF JUAN DE FUCA, HARO STRAIT, AND SAN JUAN ARCHIPELAGO

DEPTH	STRAIT OF JUAN DE FUCA			HARO STRAIT			SAN JUAN ARCHIPELAGO		
	Temp.	Cl	Fe	Temp.	Cl	Fe	Temp.	Cl	Fe
	° C.	‰	Mg./liter	° C.	‰	Mg./liter	° C.	‰	Mg./liter
Meters									
1	11.83	16.18	0.037	10.68	16.81	0.042	14.58	15.01	0.030
10	10.86	16.71	0.050	10.35	16.95	0.068	13.05	15.66	0.040
25	10.10	17.26	0.050	10.32	17.09	0.083	11.87	16.32	0.045
50	8.32	18.15	0.050	9.66	17.26	0.089	10.45	16.95	0.065
100	7.40	18.46	0.088	8.92	17.65	0.110	9.65	17.34	0.085
150-200	6.93	18.71	0.280	8.53	17.99	0.115	9.10	17.66	0.085
300				8.35	18.04	0.188			

Unpublished data of Lyman D. Phifer, phytoplanktonist for the Oceanographic Laboratories, show that there is a marked abundance of diatoms in the surface water layers of the Strait of Juan de Fuca to depths just below 25 meters. The plankton are distributed throughout the water mass in larger quantities in Haro Strait and the tidal channels of the Archipelago, and exist in still greater abundance in the estuaries of the latter.

The data in Table II indicate that the iron is actually removed from the water by microscopic plants and that iron may be an essential element for their growth. This is further substantiated by the data in Table I, which show that the iron was completely absorbed by the growth of the diatoms contained in the samples taken in East Sound.

Figure 1 shows the distribution of iron in the waters of the Strait of Juan de Fuca, Haro Strait, and the San Juan Archipelago. The bottom waters of the Strait of Juan de Fuca have a relatively greater iron content than the waters from other depths and areas. The graph illustrates the partial mixing of these waters with those of the surface layers as they reach the deeper and more turbulent condition of Haro Strait. A similar presentation of either temperature or chlorinity data would show the same result.

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Determination of Alkalinity in Boiler Waters

A Comparison of Methods

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MCKINNEY (5) questions the accuracy of the standard methods which have been used in the analysis of boiler waters and suggests a new method of calculating the distribution of the ions which he terms the "equilibrium method." In order to compare the results obtained when using the standard methods of analysis and his method, he prepared synthetic solutions and analyzed them using the A. P. H. A. and Winkler methods of analysis. In Table V, page 196 (5), he gives the results of these data and calculations, results which would indicate, especially from sample 1, that the old standard methods are open to an exceptionally large error. Since the original data are not given, one must assume that 0.02 N acid was used, and 100 cc. of the sample was used for titration. Based on these assumptions, the amount of acid necessary to titrate the synthetic solution, allowing for the slight increase in carbon dioxide above that actually added as sodium carbonate, would be 44.6 cc. for the phenolphthalein end point and 50.7 for the methyl orange end point. However, to obtain the values reported these would have been 94.9 cc. for phenolphthalein and 104.4 for methyl orange end point. Such errors are

certainly not probable in the regular A. P. H. A. titration using synthetic solutions. However, if the results reported had been miscalculated so that they were actually sodium carbonate and sodium hydroxide instead of carbonate and hydroxide as reported, a recalculation would give CO₃ = 60.8 p. p. m. against 69 calculated to be present; and OH = 123 p. p. m. against 131 calculated to be present. This agreement is within reasonable limits. If this were so, the titration figures would be phenolphthalein = 41.6 and methyl orange = 47.0 cc. of acid, which agree fairly well with the values calculated for the synthetic solutions. The use of the pH value for calculating hydrate concentration is open to much error, for this value cannot be definitely determined within an error of ±0.1, and often an error of 0.5 is possible. Assume that an accuracy of 0.1 is possible. Thus, with a solution having a pH of 11.75 as calculated in (e), page 195, the value for 11.75 and activity of 0.87 would be 6.507 millimoles of hydroxide or 260 p. p. m. sodium hydroxide. If the pH determined were 11.85, the result would be 7.127/0.87 = 8.18 millimoles of hydroxide.

TABLE I. COMPOSITION OF SYNTHETIC SOLUTIONS

Soln. no.	1	1A	1B	2	2A	2B	3	3A	3B	4	4A	4B
						<i>Millimoles per liter</i>						
NaOH	2.36	2.36	2.56	7.90	7.85	8.75	14.95	14.95	16.38	39.40	39.40	41.34
Na ₂ CO ₃	0.84	0.84	0.93	1.06	1.08	1.19	3.02	3.02	3.18	14.80	14.80	14.80
NaCl	1.00	1.00	1.00	5.00	5.00	5.00	5.00	5.00	5.00	15.00	15.00	15.00
Na ₂ SO ₄	2.46	2.46	2.46	7.00	7.00	7.00	25.60	25.60	25.60	75.30	75.30	75.30
PO ₄		0.75	0.75		1.00	1.00		3.75	3.75		3.75	3.75
SiO ₂			0.50			1.95			3.00			3.88
						<i>Parts per million</i>						
NaOH	94	94	102	316	314	352	598	598	655	1575	1575	1654
Na ₂ CO ₃	89	89	99	113	115	121	320	320	338	1568	1568	1568
NaCl	58	58	58	293	293	293	293	293	293	876	876	876
Na ₂ SO ₄	350	350	350	995	995	995	3630	3630	3630	10680	10680	10680
PO ₄		71	71		95	95		356	356		356	356
SiO ₂			30			117			181			233

or 327 p. p. m. sodium hydroxide, an error of 25.8 per cent. An error of the same order of magnitude occurs in the calculation of HCO₃⁻ in this pH range. At lower pH values the CO₃⁻ calculation is similarly affected by an error of 0.1 in the pH. This would indicate that the use of this method is certainly not to be recommended until more accurate methods of determining pH values can be placed in the hands of the plant or routine laboratory operators.

It has been known for at least the last 15 years that the alkalinity values obtained by ordinary titration methods do not give all the desirable information in regard to the solution being tested and that the additional information given by the pH value is often desirable. However, for the reasons already given, it has not been considered advisable to rely entirely on the pH value. The two methods of testing solutions give supplementary data, and neither method is absolutely independent of the other.

The A. P. H. A. and the Winkler methods of determining alkalinity have been used as standard methods for years. However, if errors as large as those reported by McKinney are probable, the methods are certainly not to be considered as standard. In order to determine the relative accuracy of the A. P. H. A., the Winkler, and the equilibrium methods, tests have been made on various solutions. These solutions were not limited, as in McKinney's work, to dilute synthetic solutions, but also included boiler waters having concentrations commonly encountered in power plants.

METHODS OF ANALYSIS TESTED

The methods of analysis tested were: (1) the alkalinity (hydrate and carbonate) determination recommended by the American Public Health Association (1) with corrections applied for phosphate when present; (2) the Winkler method for hydrate and a modification of this method for carbonate (4, 6, 7); and (3) the equilibrium method, both short and complete, recently discussed by McKinney and Hecht (3, 5). The determination of phosphate by a direct titration method was also used.

SOLUTIONS USED FOR COMPARATIVE ANALYSIS

The solutions used for the comparative analysis consisted of twelve synthetic solutions of known composition similar to boiler concentrates and eleven boiler concentrates obtained from power plants in various parts of the United States and Canada which were representative of the various types of boiler waters encountered in operating plants.

The synthetic solutions were made up by using redistilled water with low carbon dioxide content in paraffined bottles, and adding the desired reagents in definite amounts. The total carbonate was determined by evolving the carbon dioxide from a known volume of the solution, absorbing it in ascarite, and weighing. The solutions contained sodium hydroxide, sodium carbonate, sodium chloride, and sodium sulfate. After four solutions of various compositions of these salts were analyzed by the test methods, definite amounts of trisodium phosphate were added, and the solutions analyzed

again. Then definite amounts of sodium silicate were added and the solutions analyzed again. Thus results were obtained with solutions free from phosphate and silicate as well as with solutions having these salts present.

The composition of the twelve synthetic solutions in millimoles per liter and parts per million is given in Table I.

PROCEDURE IN MAKING ANALYSES

The analyses of the synthetic waters were run in duplicate by three different analysts. The solutions were titrated in Erlenmeyer flasks using approximately 0.05 *N* acid. The A. P. H. A. tests were made by titrating with phenolphthalein indicator to colorless and methyl orange indicator to the first color change. When phosphate was present, 5 cc. excess of acid were added after the methyl orange end point was reached, the solution boiled for 3 minutes, cooled, and titrated with standard sodium hydroxide, until the first appearance of a reddish color similar to the alkaline color of phenolphthalein. A blank run using distilled water and carried through all of the steps of the procedure applied to the regular samples familiarized the operator with the end point and provided the correction allowance for the excess acid added. The difference between the amount of acid used and the blank was taken as a measure of the phosphate.

The Winkler test was run by adding 5 cc., and in the more concentrated solutions 10 cc., of a standard solution of sodium hydroxide containing about 10 per cent barium chloride to the sample of boiler water in an Erlenmeyer flask. The flask was then stoppered, let stand at least 15 minutes, and then titrated with the standard acid solution until colorless with phenolphthalein indicator.

The short equilibrium method tests were run using bromocresol green and thymol blue indicators with a Hellige-Klett pH comparator modified according to McKinney and Hecht (3).

The pH value was determined by use of the hydrogen electrode. Whenever the pH value was within the range of the colorimetric pH comparator, it was also determined colorimetrically.

The solutions were analyzed for sulfate, phosphate, chloride, and silica by standard laboratory methods. These determinations were made by only one operator.

The boiler waters were run by only two operators and not in duplicate. The agreement of the results obtained by the two operators was within the experimental error in the majority of the boiler water tested. Consequently duplicate analyses were not run.

CALCULATIONS OF RESULTS

A. P. H. A. METHOD. The amount of acid used to reach the phenolphthalein end point is designated as *P*, and the total required to reach the methyl orange end point as *M*. *N* represents normality of the acid, *V* the volume of solution tested, and PO₄ the phosphate content in p. p. m.

The calculations involved in the absence of phosphate are as follows:

$$\text{Na}_2\text{CO}_3, \text{ p. p. m.} = \frac{106 \times 1000 \times N}{V} (M - P) \tag{1}$$

$$\text{NaOH, p. p. m.} = \frac{40 \times 1000 \times N}{V} (2P - M) \tag{2}$$

If phosphate is present, the calculations are based on the fact that when a solution containing hydrates, carbonates, and phosphates of sodium is titrated with acid to the *P* and *M* end points, the amount of acid required between the *P* and *M* end points is equal to one-half the carbonate and one-third the phosphate (2).

The calculations for hydrate and carbonate in the presence of phosphate are as follows:

$$\text{NaOH, p. p. m.} = \frac{40 \times 1000 \times N}{V} (2P - M) \tag{2}$$

$$\text{Na}_2\text{CO}_3, \text{ p. p. m.} = \frac{106 \times 1000 \times N}{V} \left(M - P - \frac{\text{PO}_4 \times V}{95 \times 1000 \times N} \right) \tag{3}$$

WINKLER METHOD. If the amount of acid necessary to titrate the solution after adding a definite volume of standard sodium hydroxide solution containing barium chloride is designated as *Pw*, and *B* represents the amount of acid needed to neutralize the standard sodium hydroxide added, then

$$\text{NaOH, p. p. m.} = \frac{40 \times 1000 \times N}{V} (Pw - B) \tag{4}$$

$$\text{Na}_2\text{CO}_3, \text{ p. p. m.} = \frac{106 \times 1000 \times N}{V} \left(M - P - \frac{\text{PO}_4 \times V}{95 \times 1000 \times N} \right) \tag{5}$$

During the preparation of this material, R. W. Fisher, of Baltimore, called the attention of the author to an error in this method which explains why the carbonate determined in this manner tends to be low when phosphate is present. In the ordinary titration to the *P* end point, all of the hydroxide, one-half of the carbonate, and one-third of the phosphate are supposed to be titrated. Thus, when the hydroxide determined by the Winkler method is subtracted from this amount, the remainder should be one-half of the carbonate and one-third of the phosphate. If the phosphate is determined, the carbonate can be calculated. However, unless the pH of the solution is above 12, there is less than one-third of the phosphate titrated, since it will not be completely converted to trisodium phosphate below a pH of 12. This means that

when one-third of the phosphate is subtracted, the carbonate will be low.

SHORT EQUILIBRIUM METHOD. The sodium hydroxide is determined by the equation

$$\text{pH} = \frac{\log \text{OH p. p. m.}}{17} + 11 \tag{6}$$

$$\text{NaOH, p. p. m.} = \frac{\text{OH} \times 40}{17} \tag{7}$$

The sodium carbonate is determined by the equation:

$$\text{CO}_3, \text{ p. p. m.} = (V_2 - V_1) 12.32 - 0.813 - 0.626 \text{ PO}_4 \text{ (p. p. m.)} \tag{8}$$

when $V_2 - V_1 =$ cc. of 0.02 *N* acid necessary to titrate 100 cc. of solution from a pH of 8.5 to 5.0.

$$\text{Na}_2\text{CO}_3, \text{ p. p. m.} = \frac{\text{CO}_3 \times 106}{60} \tag{9}$$

The complete equilibrium method calculations are described in detail by McKinney (5). The sodium hydroxide from the pH value is calculated from the same formula as the one used in the short method, Equations 6 and 7, except that allowance is made for the fact that the activity is not equal to 1. To determine the activity, a knowledge of the composition of the solution is essential. In these tests this calculation is made only on the synthetic solutions, since there are not sufficient data available to calculate the activity in the boiler waters.

DETERMINATION OF PHOSPHATE BY DIRECT TITRATION. The amount of alkali necessary to back titrate the A. P. H. A. test sample which has had 5 cc. excess of acid added after the *M* end is reached, is designated by *A*. *B* equals the amount of acid used to back titrate the blank, and *Nc* equals the normality of caustic solution used.

$$\text{PO}_4, \text{ p. p. m.} = \frac{95 \times 1000 \times Nc}{V} (A - B) \tag{10}$$

RESULTS OF ANALYSES

The average results of the analyses on the synthetic solutions and the boiler waters are given in Table II. Table III shows the per cent error in the sodium carbonate and sodium hydrate contents for all the solutions tested.

The per cent error in the sodium carbonate content of the synthetic solutions illustrates that the A. P. H. A. and the short equilibrium method both show good agreement with the actual content. In order to check this further, the average ($V_2 - V_1$) and ($M - P$) readings were compared. This is done

TABLE II. AVERAGE Na_2CO_3 AND NaOH BY DIFFERENT METHODS IN SYNTHETIC SOLUTIONS AND BOILER WATERS
(Parts per million)

SAMPLE	BY CO_2		A. P. H. A.	WINKLER	SHORT		NaOH	A. P. H. A.	WINKLER	LONG	
	EVOLUTION				EQUILIBRIUM	EQUILIBRIUM ^a				EQUILIBRIUM	FROM pH VALUE
1	89	84		87	94	89	94	97	96	89	97
1A	89	86		42	91	89	94	96	110	127	144
1B	99	86		61	96	99	102	106	115	113	127
2	113	124		116	116	113	316	310	309	226	232
2A	115	121		70	120	115	314	305	321	282	330
2B	121	126		115	129	121	352	348	352	400	495
3	320	323		347	329	320	598	594	584	425	580
3A	320	323		292	321	320	598	596	619	588	870
3B	338	327		382	349	338	655	657	648	517	715
4	1568	1542		1560	1562	1568	1575	1605	1595	1128 ^b	
4A	1568	1543		1485	1603	1568	1575	1581	1622	1600	
4B	1568	1505		1773	1592	1568	1654	1685	1593	1600	
101	16	28		3	27			24	39	39	
102 ^c	8	58		41	29			66	73	127	
103 ^c	5	28		14	33			43	48	49	
104	30	44		3	41			343	361	350	
105	26	81		49	50			194	199	179	
107	24	68		0	68			157	185	127	
108	493	506		536	539			1482	1472	1665	
109	6675	6865		7165	7215			1797	1695	1010	
110	648	705		786	732			969	939	588	
111	495	536		591	587			573	556	310	
112 ^c	25	40		0	42			15	30	0	

^a About 3 per cent of the carbonate will be as bicarbonate. However, for simplicity it is included in the sodium carbonate figure. Since the sodium carbonate is calculated from the carbon dioxide obtained by evolution, results are same as those in column 1.

^b Too high a concentration of salts to calculate activity with any degree of accuracy

^c In low carbonate-ion concentrations the error is necessarily large.

in Table IV. The difference between $(V_2 - V_1)$ and $(M - P)$ is calculated in per cent of $(V_2 - V_1)$. The maximum per cent error of any one determination from the average for $(V_2 - V_1)$ and $(M - P)$ is also shown. These results show very good agreements, and indicate that for the waters analyzed the equilibrium and A. P. H. A. methods are equally satisfactory. In the synthetic solutions the $(V_2 - V_1)$ average maximum error was 1.9 per cent, whereas that of the $(M - P)$ reading was 0.6 per cent. For the boiler waters the errors were 4.4 and 3.6, respectively, thus showing that the A. P. H. A. determination with the use of much less expensive equipment gave results as close as the method involving the use of the color comparator.

TABLE III. ERROR IN Na_2CO_3 AND NaOH CONTENT FOR SOLUTIONS TESTED

WATER	ERROR IN Na_2CO_3 CONTENT			ERROR IN NaOH CONTENT		
	A. P. H. A.	Winkler	Short equilibrium	A. P. H. A.	Winkler	Short equilibrium
	%	%	%	%	%	%
1	-5.5	-2.5	-5.5	3.2	2.1	-5.3
1A	-3.4	-53.0	2.2	2.1	17.0	35.0
1B	-13.0	38.0	3.0	3.0	13.0	11.0
2	10.0	2.7	2.7	1.9	-2.0	-28.4
2A	6.2	-39.0	4.3	-2.9	2.2	-10.1
2B	4.1	-4.9	6.6	-1.1	0.0	+29.0
3	1.0	8.5	3.0	-0.6	-2.3	-29.0
3A	1.0	-8.7	0.3	-0.3	3.5	-1.6
3B	-2.9	13.0	2.9	+0.3	-1.1	-21.0
4	-1.7	-0.1	0.1	1.9	1.2	-28.0
4A	-1.6	-5.3	2.2	0.4	3.0	1.6
4B	-4.0	+13.0	1.5	1.9	-3.6	3.3

TABLE IV. COMPARISON OF ACCURACY OF DETERMINING $(V_2 - V_1)$ AND $(M - P)$ VALUES IN ALL WATERS

WATER	$(V_2 - V_1)$ Av.	$(M - P)$ Av.	$\frac{(V_2 - V_1) - (M - P)}{(V_2 - V_1)}$ %	$(V_2 - V_1)$ MAX. ERROR FROM Av.	$(M - P)$ MAX. ERROR FROM Av.
				%	%
1	1.67	1.70	-1.8	4.8	4.8
1A	3.35	3.31	1.2	4.8	0.6
1B	3.42	3.27	+4.3	3.8	10.0
2	2.35	2.52	-7.0	15.0	7.0
2A	4.37	4.52	-3.2	4.1	1.7
2B	4.63	4.65	-0.4	2.6	0.0
3	3.28	3.27	+3.0	3.6	1.8
3A	7.20	7.20	0.0	7.5	2.2
3B	7.25	7.24	0.1	0.8	0.1
4	7.83	7.77	0.8	0.5	0.2
4A	9.77	9.81	-0.4	2.3	0.1
4B	9.71	9.57	-0.2	1.9	0.6
			Av. -0.6	4.3	2.5
101	1.59	1.64	-3.1	3.8	2.4
102	0.70	1.19	-70.0	0.0	0.5
103	0.67	0.57	+15.0	3.0	0.7
104	3.23	3.43	-6.1	1.2	0.9
105	1.26	1.63	-23.0	3.2	1.2
107	2.52	2.72	-8.0	7.0	4.5
108	2.90	2.55	1.4	7.0	7.6
109	14.15	13.85	2.1	1.8	1.1
110	3.65	3.55	2.7	1.3	0.6
111	2.94	2.71	7.9	10.5	4.1
112	0.83	0.80	3.8	3.8	0.0
			Av. -7.0	3.9	2.3

In order to understand why there should be such close agreement of these two methods, it is only necessary to compare the formulas for calculating the results. The A. P. H. A. method, when corrected for phosphate, gives the following equation:

$$\text{Na}_2\text{CO}_3, \text{ p. p. m.} = \frac{106 \times 1000 \times N}{V} \left(M - P - \frac{\text{PO}_4 \times V}{95 \times 1000 \times N} \right) \quad (3)$$

If $N = 0.02$ and $V = 100$, then:

$$\text{Na}_2\text{CO}_3, \text{ p. p. m.} = 21.2(M - P) - 0.111 \text{ PO}_4, \text{ p. p. m.} \quad (11)$$

or $\text{CO}_3, \text{ p. p. m.} = 12.0(M - P) - 0.63 \text{ PO}_4, \text{ p. p. m.}$

Equation 8 for the carbonate by the short equilibrium method is as follows:

$$\text{CO}_3, \text{ p. p. m.} = 12.32(V_2 - V_1) - 0.813 - 0.626 \text{ PO}_4, \text{ p. p. m.} \quad (8)$$

The results tabulated in Table IV show that the $(V_2 - V_1)$ and $(M - P)$ readings are almost identical for the synthetic solutions and show good agreement in the boiler waters. The maximum difference between these two equations should come in low concentration. Thus, if the figures obtained in water 112, $(V_2 - V_1) = 0.83$ and $(M - P) = 0.80$, were substituted in their respective formula with $\text{PO}_4 = 0$, the results are as follows:

$$\begin{aligned} \text{CO}_3 \text{ by A. P. H. A.} &= 22.4 \text{ p. p. m.} \\ \text{CO}_3 \text{ by equilibrium} &= 23.0 \text{ p. p. m.} \end{aligned}$$

which agrees within the experimental error. If phosphate is present as in water 1A, then:

$$\begin{aligned} \text{CO}_3 \text{ by A. P. H. A.} &= 48.4 \text{ p. p. m.} \\ \text{CO}_3 \text{ by equilibrium} &= 51.6 \text{ p. p. m.} \end{aligned}$$

which agrees within the experimental error. The calculation of the carbonate by the short equilibrium method applies corrections to the older method which are less than the experimental error. Consequently, the results agree very closely with those obtained by the older method.

The carbonate as determined by the combination of the Winkler method with the P determination of the A. P. H. A. method, gave good results in the absence of phosphate and silicates. The presence of phosphate tended to decrease the amount found, whereas the addition of silicate increased the carbonate determined.

The reported carbonate in the boiler waters was very interesting. In samples 108, 109, 110, and 111, the results are fairly close to the actual carbonate present. Any one of the methods appears to give accurate results. These boiler waters contain appreciable amounts of alkalinity, low organic matter, and no phosphate. They are typical of the boiler waters found in lower pressure industrial plants. The results on all the other boiler waters showed that none of these methods gives concordant carbonate results in low concentrations.

The sodium hydroxide results obtained on the synthetic waters by the A. P. H. A. method were very accurate. The Winkler method also gave very good results. The short equilibrium method gave very erroneous results. In the absence of phosphate, the results were low. With phosphate present, the results tended to be higher. One would not expect the hydrate to be correct, since it is assumed that the activity is equal to 1, and in most of the waters tested it is less than 0.85. This would tend to give low results. At the same time a large error is introduced with only a small variation in pH determination. Thus, an error of 0.1 in pH means an error of 25 per cent. In the boiler waters 108, 109, 110, and 111, the Winkler and the A. P. H. A. methods give good results for the hydrate. These are the clean waters which gave good carbonate results. The short equilibrium method gives low results on the boiler waters 109, 110, 111, and 112. It is almost impossible to calculate the activity coefficients for these solutions with any degree of accuracy, and consequently this correction cannot be applied. In general there is nothing in these results to show that the determination of pH values gives anything more than an approximation of the hydrate content unless corrected for activity, and then in the presence of phosphate or silicate the values would be too high.

As some of the waters tested contained phosphate, the amount present was determined both by the standard laboratory procedure and by the back-titration method. It was found that in the synthetic solutions the back-titration method gave very good agreement with the standard procedure, whereas in the boiler waters the agreement was poor in most cases. It seems as though the presence of organic matter in the boiler waters influences the results obtainable by back titration and introduces errors which cannot be compensated for in the calculation of the results.

CONCLUSIONS

The conclusions to be reached from digesting the results of these analyses are:

1. The A. P. H. A. and Winkler methods give reliable hydrate content in the absence of high silica and organic matter. In the presence of organic matter the Winkler method appears to be the most reliable.

2. The determination of hydrate from the pH value gives erroneous results.

3. The carbonate determined by the A. P. H. A. method is accurate in the absence of organic matter. However, in boiler waters having the sodium carbonate below 50 p. p. m. this method is not reliable.

4. The determination of carbonate using the short equilibrium method gave results which averaged about the same as those obtained by the A. P. H. A. method.

5. The carbonate determined by the carbon dioxide evolution method gave the most reliable results for carbonate.

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An Inexpensive Low-Temperature Thermostat

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THE low-temperature thermostat described in this paper, although inexpensive to construct and to operate, has been found to be accurate and reliable. Liquid ammonia is used as the cooling agent for temperatures between 7° and -25° C. This substance is cheap, readily available, and because of its exceptionally large heat of vaporization per unit weight, cools economically. Ice is used to cool the bath for temperatures between 7° and room temperature. The method of applying the cooling agent differs from the usual practice in that the heat is conducted away from the bath to the cooling agent by means of a copper rod soldered through the wall of the bath, which is constructed of copper. The cooling of the bath liquid is thus accomplished by transfer of heat to the container wall, rendering the use of a cooling coil or other device in the bath itself unnecessary.

DESCRIPTION OF APPARATUS

The bath and its associated apparatus are illustrated diagrammatically in Figure 1. The bath itself consists of a copper tank, *a*, made by soldering one end of a section of copper tubing 7.5 inches (19.05 cm.) long and 3.5 inches (8.89 cm.) inside diameter into a groove turned in a copper disk 4.5 inches (11.43 cm.) in diameter. The walls and bottom of the bath are 0.125 inch (0.32 cm.) thick. A 1-inch (2.54-cm.) hole is drilled in the wall of the bath 2.5 inches (6.35 cm.) from the top, and through this hole is soldered a 1-inch (2.54-cm.) copper rod, *b*, so that it extends 0.5 inch (1.27 cm.)

downward 2.5 inches (6.35 cm.) from the wall of the bath, passes through a cork, *c*, and extends down 8 inches (20.32 cm.) below the bend. The bath and that portion of the rod between it and the cork are carefully lagged with 1.5 inches (3.81 cm.) of hair felt (not shown). The lagging is somewhat thinner between the rod and the bath to allow clearance for the vacuum bottle. Kerosene is used as the bath liquid.

The bath is cooled continuously by inserting the copper rod into a 500-cc. silvered vacuum bottle, *d*, containing liquid ammonia, or into a beaker of ice and water. The cork, *c*, fits loosely into the neck of the bottle. Heat is supplied

intermittently by one or two 21-candle power automobile headlight bulbs, *f* and *f'*, as conditions may require. The switches, *o* and *o'*, are arranged to permit the use of one or both bulbs. The bulbs, which are lighted by a standard 6-volt storage battery, are mounted with special clamps of brass strap, *g* and *g'*, which pass around the base of the bulb and are soldered to the 0.125-inch (0.32-cm.) copper rod, *h*, which passes through the cork, *i*, and forms one side of the lamp circuit. Copper wires, *j* and *j'*, are soldered to the other contact of the bulbs and pass through the cork to the insulating bracket, *k*. The lamp circuit is controlled by the 250-ohm relay, *l*, the primary circuit of which is operated by a conventional gas type thermoregulator which consists of a gas-filled 20-cc. bulb, *m*, connected by a small-bore capillary to a closed-end manometer of slightly more than barometric height, which was carefully boiled out after being filled with

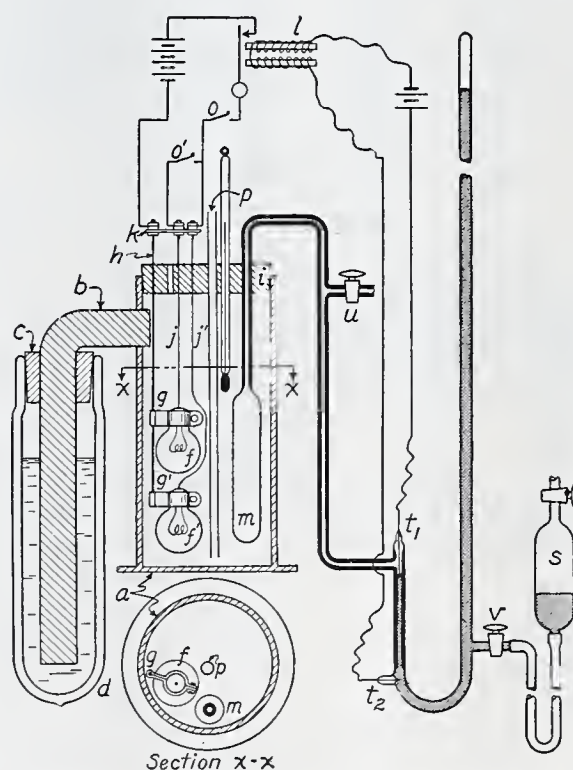


FIGURE 1. DIAGRAM OF LOW-TEMPERATURE THERMOSTAT

pure mercury. Tungsten leads tipped with platinum are sealed through at t_1 and t_2 . The circuit is made and broken by the rise and fall of the mercury in the capillary at the tip of t_1 . The dead space above the mercury at t_1 and in the connecting capillary is so small that variations in room temperature do not perceptibly affect the setting of the thermoregulator. The cross section at $x-x$, shown immediately below the bath in Figure 1, shows the arrangement of parts in the other plane. Most of the bath space is left free for other apparatus.

Figure 2 is a photograph of the bath, vacuum bottle, and wooden stand used to support them. The bottle rests on a movable shelf which may be removed at any time to permit lowering of the bottle. The picture shows the lagging and the method of securing it with metal straps ordinarily used for fastening lagging to steam pipes. The large cork, i , which closes the top of the bath and through which the lead wires, tubes, etc., pass, is bolted to a horizontal cross-piece (not shown) which forms part of the frame which supports the manometer and other equipment. The cork and other apparatus are thus supported independently of the bath which can be lowered to expose the apparatus by simply removing the stand.

Because of the small size of the bath, no mechanical stirrer is used, but instead dried air is passed in through the tube p and allowed to bubble up through the bath liquid. This has been found quite satisfactory. Precooling of this air would make it possible to operate at somewhat lower temperatures with a given cooling agent.

The operation of the apparatus is as follows: The bath is brought to the desired temperature by immersing the rod in liquid ammonia or ice while the cock, u , is open. The height of the mercury in the manometer is then adjusted by means of the leveling bottle, s , until it makes contact at t_1 , the cocks, u and v , are closed, and the heaters turned on. The bath will then hold the desired temperature. Additional ammonia or ice can be added at any time without interfering with the operation of the thermostat. In cooling the bath initially to temperatures below 0°C ., some time and liquid ammonia can be saved by precooling the bath liquid. This is done by immersing the kerosene in an ice bath before it is poured into the thermostat.

DISCUSSION

The bath as described has been used only with liquid ammonia and ice, but there is no apparent reason why it could not be used equally well with other cooling media, for example, liquid air or carbon dioxide snow in acetone, and thus be made to operate at lower temperatures than are possible with liquid ammonia. The practical lower limit, using ammonia, is about -25°C ., but the limit would not approach the temperatures of liquid air and carbon dioxide snow as closely as it does that of liquid ammonia, owing to increased heat losses at lower temperatures. The bath has been operated at several temperatures between 0° and -25°C ., using liquid ammonia, and at 6.75° , 9° , and 19°C ., using ice. The range between room temperature and -25°C ., is thus readily covered with the two cooling agents, ice and liquid ammonia. No change in the apparatus is required when cooling agents are changed. The highest practical operating temperature with any cooling medium is reached when the bath cools so rapidly that the heaters must operate almost continuously to maintain that temperature. With two bulbs in use, it is possible to operate at higher temperatures with a given cooling agent, and by using one or two bulbs as necessary the heating and cooling periods can be made more nearly equal.

The ammonia consumption is small, 400 cc. being sufficient

to cool the bath from 15° to -15°C . and maintain it at the latter temperature for 5 hours. Starting with the bath already down to temperature, a single filling suffices for a day's run of about 7 hours. The apparatus is being used under a fume hood and the ammonia fumes have given no trouble. For operation in the open air the cork, c , should be made to fit tightly and a tube passed through it at the side through which the ammonia fumes could be carried off as desired. Care must be exercised when placing the bottle of ammonia around the copper rod, as the ammonia boils violently when it first touches the warm rod.

The temperature change of the bath during its heating or cooling period was imperceptible on a pentane thermometer, and an attempt was made to follow it with a copper-constantan thermocouple. The couple was made of fine wire

and was placed in direct contact with the bath liquid to reduce the lag as much as possible. The e. m. f. readings were made with a Leeds and Northrup Type K potentiometer and galvanometer to 1 microvolt. Although these readings could hardly have an absolute accuracy of 1 microvolt, if all errors affecting the instrument are assumed constant over the brief interval of a heating or cooling period, then the change in e. m. f. should be accurate to about 1 microvolt (0.027°C .). Of thirteen readings taken with the bath operating at -10°C ., a readable difference was observed in only one case in which the e. m. f. changed 1.5 microvolts between the start and end of a heating period (67 seconds). Similar results were obtained with the bath operating at -19°C . Out of eleven determinations one readable difference of 5 microvolts was observed, all the others showing no perceptible variation between the start and end of a heating or cooling period. The two observations showing variation were probably due to some extraneous cause, especially since both showed a change of e. m. f. in the direction opposite to that which would be expected. The twenty-four determinations were made under a variety of conditions, with the vacuum bottle half filled with ammonia, with the bottle full, with one bulb in use, with both in use, with the thermocouple junction near the top, and with the junction near the bottom.

The bath was explored with the thermocouple junction to determine whether adequate stirring was being obtained. Of five readings taken at widely separated points in the bath, a variation of ± 1 microvolt was observed, corresponding to a temperature variation of $\pm 0.03^\circ\text{C}$. Although this could perhaps be improved by mechanical stirring, it is entirely adequate for many purposes.

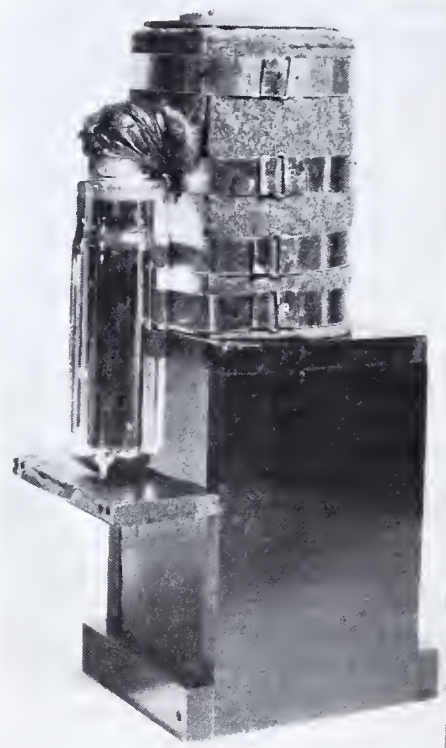


FIGURE 2. THERMOSTAT BATH AND STAND

Determination of Oil Content of Pecans

New Sulfuric Acid Digestion Method

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THE gravimetric ether extraction methods now used for the quantitative determination of the oil or fat content of pecans have several disadvantages. First, they are time-consuming, a factor to be considered when many tests are to be made; second, ether solvents extract other materials besides oil; and third, it is practically impossible to drive off all moisture without oxidizing some oil.

A new method for extracting oil from pecans has been developed which overcomes the foregoing disadvantages, at least in part. It is based upon the same procedure as is applied in the Babcock cream test. Pecan oil in a pure state is liberated from the nut meats by dilute sulfuric acid at a certain temperature. With the ether extraction method, from 21 to 22 hours are necessary for making the test, as compared with 30 minutes with the new method. Aside from the considerable time saved by the new method, some progress has been made in overcoming error. Preliminary tests indicate that the method gives promise of equal value in the determination of oil in nuts and seeds of other plants, such as peanuts, walnuts, coconuts, cotton seed, flax seed, etc.

EQUIPMENT AND MATERIALS

1. Fifty per cent, 9-gram, so-called "6-inch cream-test" bottles, used in the Babcock cream test. They have a bulb capacity of approximately 45 cc.
2. A centrifugal machine equipped with a Babcock-test attachment and geared to a speed of 800 to 1000 revolutions per minute.
3. A constant-temperature bath, large enough to hold all the bottles used in one run, deep enough to come within 0.5 inch (1.27 cm.) of the top of the test bottle, and capable of maintaining temperatures of 55° and 65° C.
4. Sulfuric acid, with a specific gravity of approximately 1.84, diluted 1.5 to 1 part of water.

EXPERIMENTAL PROCEDURE

The pecans used for this work were collected from orchards in Texas and Louisiana and consisted of several of the more common varieties. These nuts were cracked and stored in tightly sealed bottles; then, as needed for experimental purposes, were very finely ground with the nut-butter cutter in a Russwin food chopper, and used immediately.

Moisture determinations were made on all samples of nuts by placing a 10-gram sample of finely ground nut meats in the vacuum oven at 65° C. for 5 hours at approximately 12.55 pounds vacuum. All calculations were based on oven-dried samples.

All oils used for comparison were tested for oxidation, using Kreis' test for detection of oxidation. Any oil found to be oxidized was discarded.

Four grams of the finely ground nut meats were weighed and transferred into a dry cream-test bottle (this can be accomplished by cutting off the stem of a 4-inch (10.16-cm.) glass funnel and holding it in position over the test bottle). Next 35 cc. of dilute (1 to 1.5) sulfuric acid were added and the bottle placed in the water bath for 15 minutes at 65° C. (a higher temperature will give a dark color to the oil). The bottle was shaken occasionally to aid digestion of the nut meats, and was then transferred to the centrifuge, counter-

balanced, and after the proper speed (800 to 1000 r. p. m.) had been attained, whirled 5 minutes. The bottle was filled to the neck with dilute sulfuric acid and whirled 3 minutes. More acid was added until the liquid column approached near the top graduations of the scale, and the bottle whirled 1 minute. The bottle was transferred back to the water bath for 10 minutes at 55° C. With the aid of dividers or calipers, the spaces occupied by the oil column from its lower surface to the top of the upper meniscus were measured.

The per cent oil can quickly be calculated using the formula:

$$\frac{\text{Spaces oil occupied in test bottle}}{\text{Spaces 1 gram oil occupied} \times \text{wt. of sample}} \times 100 = \% \text{ oil}$$

As the cream-test bottles used are graduated to read in terms of butter fat and not pecan oil, it was necessary to determine the spaces occupied by 1 gram of oil and calculate the per cent of oil from the factor found. The spaces occupied by 1 gram of oil were determined as follows: a cream-test bottle was filled to the neck with sulfuric acid (1 to 1.5) and pecan oil was added to the first graduation of the bottle, then the bottle was placed in the water bath for 10 minutes at 55° C., transferred to the centrifuge, and whirled 3 minutes. The bottle was again placed in the water bath at 55° C. for 10 minutes and the space occupied by the upper meniscus of the oil read. Now the test bottle was placed on the analytical balance and 3 grams of oil accurately weighed into it; then it was placed in the water bath for 10 minutes at 55° C., transferred to the centrifuge, and whirled for 1 minute after the proper speed had been attained, and again placed in the water bath for 10 minutes at 55° C. With the aid of calipers, the spaces occupied by the 3 grams of oil were measured from its lower surface to the top of the upper meniscus. The spaces occupied by the 3 grams of oil divided by 3 equals the space occupied by 1 gram of oil. By using the factor thus obtained, the per cent oil is readily calculated.

TABLE I. SPACES OCCUPIED BY OIL FROM DIFFERENT VARIETIES OF PECANS

(1 gram of oil at 55° C.)	
VARIETY OF PECAN	SPACES OCCUPIED
Schley	11.15
Moneymaker	11.16
Pabst	11.17
Success	11.22
Stuart	11.23

TABLE II. COMPARATIVE RESULTS BY PETROLEUM ETHER EXTRACTION AND NEW METHOD

VARIETY OF PECANS	OIL BY NEW METHOD	OIL BY PETROLEUM ETHER EXTRACTION
	%	%
Schley	77.20	77.80
	76.34	76.93
Success	74.35	74.10
	75.04	74.20
Stuart	73.77	73.11
	75.10	74.40
Pabst	72.52	72.89
	73.96	74.43
Moneymaker	76.39	76.25
	77.58	77.73

The space factor is not the same for all varieties of pecans. Table I shows the spaces occupied by 1 gram of oil at 55° C.

for several varieties of nuts. From this table it is evident that the spaces in the cream-test bottle occupied by 1 gram of oil vary slightly with each variety. The average of all the tests was 11.18 spaces occupied by 1 gram of oil. Using the factor 11.18 gives results very near to those obtained by the gravimetric method, as seen in Table II. Greater accuracy, however, can be obtained by using the individual factor for each variety of nuts, but this does not seem necessary for most work. More work needs to be done at this point and will be undertaken when time permits.

TABLE III. CHEMICAL AND PHYSICAL CHARACTERISTICS OF PECAN OIL EXTRACTED BY EXPRESSION, PETROLEUM ETHER, AND NEW METHOD

METHOD OF EXTRACTING	IODINE No. (WIJS METHOD)	(Stuart variety)		SPECIFIC GRAVITY (WESTPHAL BALANCE)	COLOR
		REFRACTIVE INDEX (ABBÉ RE-FRACTOMETER)	SAPONIFICATION No.		
Expressed	102.86	1.4670	189.89	0.9190	Light golden
Petroleum ether	103.27	1.4670	187.80	0.9190	Light golden
New method	103.83	1.4670	189.95	0.9190	Colorless

The percentages of oil as determined by the petroleum ether extraction and the new method are shown in Table II. Samples of each variety were collected from two different localities and the determinations made in duplicate. The results are found to compare favorably.

Table III shows a comparison of the physical and chemical characteristics of pecan oil extracted by expression and by the two foregoing methods. This table shows the oil from the different methods to have practically the same properties. The refractive index and specific gravity were the same with all three methods. The iodine number and saponification number were highest with the new method, indicating that a purer oil was obtained by this method.

ACKNOWLEDGMENT

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Graphic Calculations in Water Analyses

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THE facts that the existing methods for calculating the elements and radicals present in mineral waters into certain hypothetical combinations are many and diverse, rendering the results of such calculations confusing and not readily comparable one with the other, and that modern chemical knowledge fully justifies no such calculations, are diverting the general tendency toward the ionic form of stating the results of water analysis.

The practice of combining the ions, however, still finds extensive application in industry, and various schemes have been evolved whereby these calculations are reduced to a routine applicable by the operator with limited chemical training.

The use of milligram equivalents (or reacting values) in water analyses has long been practiced (1, 4), and an elaboration on the use of equivalents has been made by graphically representing the results of analysis (2, 3). These graphic representations have been employed for a number of years in publications of the U. S. Geological Survey. The use of equivalents may be further extended to the length of integrating the hypothetical combinations by mechanical methods.

In the method herein advocated, a determination of calcium, magnesium, carbonate, sulfate, and chlorine is made. The results, stated as parts per million, are converted to the milligram equivalents per kilogram (Stabler's reacting values, 4) by multiplying by the reciprocals of the combining weights of the respective ions. The results being thus con-

verted, any ion may be combined with any other ion in numerically equal quantities. The advisability of determining the sodium and potassium is contingent upon the accuracy desired, and when sodium and potassium are not determined, such an amount of sodium is "written in" as will cause the sum of the equivalents of the acid radicals to be exactly equal to the sum for the bases. The probability of the two sums balancing when all of the ions are determined is very small, and the small difference usually existing is distributed so as to effect a balance.

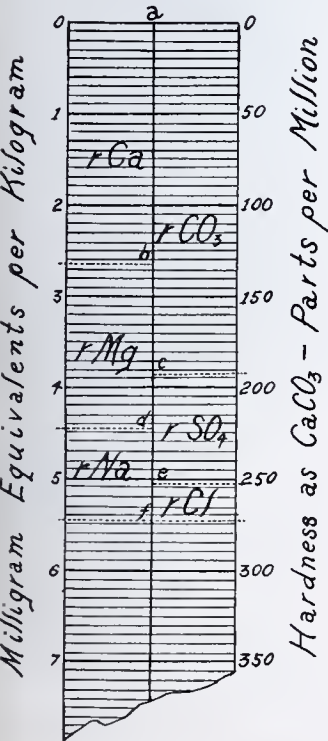


FIGURE 1

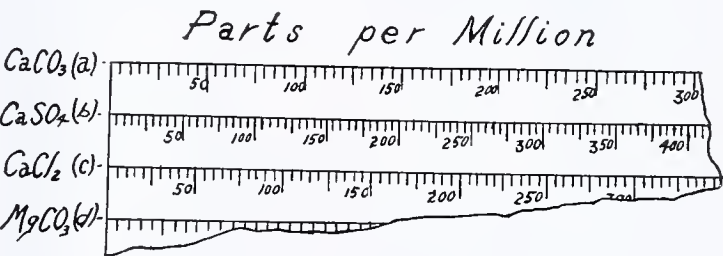


FIGURE 2

The equivalents of the positive and negative radicals, being thus adjusted, are then consecutively laid out on prepared coordinate paper (calibrated in milligram equivalents) on either side of a central line (Figure 1). The length on the graph representing an ion may be called the "reacting length" of that ion. Since linear distance on the graph is quantitatively proportional to the equivalents of the ions, it is also proportional to the equivalents of the compounds. All radicals lying laterally contiguous are combined, and the compounds supposedly present in the sample may thus be instantly visualized. The failure of two radicals to lie laterally adjacent connotes the absence of the compound composed of those two radicals.

The results as read from this graph are in terms of milligram equivalents and necessitate a conversion into the desired units. A series of graphic scales, one for each possible compound, are constructed for this purpose (Figure 2) and may be used indefinitely.

To convert the calcium carbonate, distance ab (Figure 1), the reacting length of the calcium carbonate, is transferred to scale a (Figure 2) by means of a pair of dividers, and the result is read directly in terms of parts per million of calcium carbonate. The length representative of 1 part per million of calcium carbonate (scale a) may be called the "factor length," and bears a ratio to the length representing 1 milligram equivalent on the graph, equal to the reciprocal of the factor for converting the milligram equivalent of calcium carbonate into p. p. m. of that compound. The factor length is determined by dividing the reacting length unit by this combination factor. Foulk (4) presents a discussion and a list of these combination factors. All other scales are made and the conversions executed in accordance with the foregoing procedure. The scales may be adjusted to give results in any unit desired, such as grains per gallon, pounds per 1000 gallons, etc.

When the linear counterpart of 1 milligram equivalent is a suitable length, for example 2 or 3 cm., the method may be applied without resort to graph paper. The numerical react-

ing values of the ions may be converted into the reacting lengths by the use of a vernier slide micrometer. These lengths are plotted on either side of a straight line drawn on a clean sheet of paper, and the conversion to the desired units made with dividers and the scales as usual.

The method is, of course, independent of the system or order of combining the radicals, the order employed above being arbitrarily selected for the purpose of demonstrating the method. The accuracy of this method varies directly with the length taken as unity in the graph.

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Pressure Pump for Circulating Gases in a Closed System

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IN AN investigation of the action of oxygen on low-temperature tar when recirculated through the material in a closed system, it was necessary to devise a pressure pump able to overcome the strong resistance created by the viscous column of tar through which the gas was to be forced. To this end, a non-mechanical pump operated by an external

water-pump through a mercury medium was constructed which would circulate 6 to 20 liters of gas per hour and which would operate day and night without attention. It has an advantage over other pumps described in the literature in its simplicity of design, or in its lack of solid moving parts and bearing surfaces. The underlying principle is somewhat similar to that of the pump described by Maass (1), but the construction is more compact and the operation less complicated.

The water-pump is connected to e , as in Figure 1. The suction produced reduces the pressure in f , a , and b which causes the mercury to rise in a and b and to go down in c and d .

When the level of the mercury in c reaches point i in b , a difference of pressure between atmospheric and that obtaining in voids of f , a , and b greater than the height of the mercury slug in b , is quickly established. The result is that the slug is shot forcibly into f , thus relieving the vacuum in e , f , and a . The mercury level in a therefore drops suddenly, forcing the level in d upward. At the same time the air intake is cut off by c 's filling with mercury as before, and the cycle repeats itself. The pulsating motion of the mercury level in d , together with the valve arrangement g and h , makes circulation of the gas through the closed system possible. Tube e is filled with glass beads and glass wool to trap stray globules of mercury.

The capacity of the stroke in d is affected by changes in diameter of a ; for a larger diameter of the latter more mercury is raised per unit height and consequently more drawn from d . Tube b is necessarily small if the slug of mercury is to be kept from breaking and hindering air admission through c . The return to atmospheric or nearly atmospheric pressure of voids in a and c can be expedited by multiplying b by two or more. For the same reason, the connection of e with the water-pump should be short and should not contain a safety-trap in series. None, in fact, is required in this apparatus. The presence of an unnecessary amount of space to be evacuated and returned to the higher pressure merely lowers the effectiveness of the pump—that is, the larger this space the more there is to be filled with air in the short time elapsing between the shooting of the slug and the cut-off of air-intake through c .

Likewise the space between the valves and pump—that is, the space above the mercury level in d at top of stroke and connecting line—should be small, so that only a very little of the stroke is wasted in compression before the valve operates.

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RECEIVED January 29, 1932. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

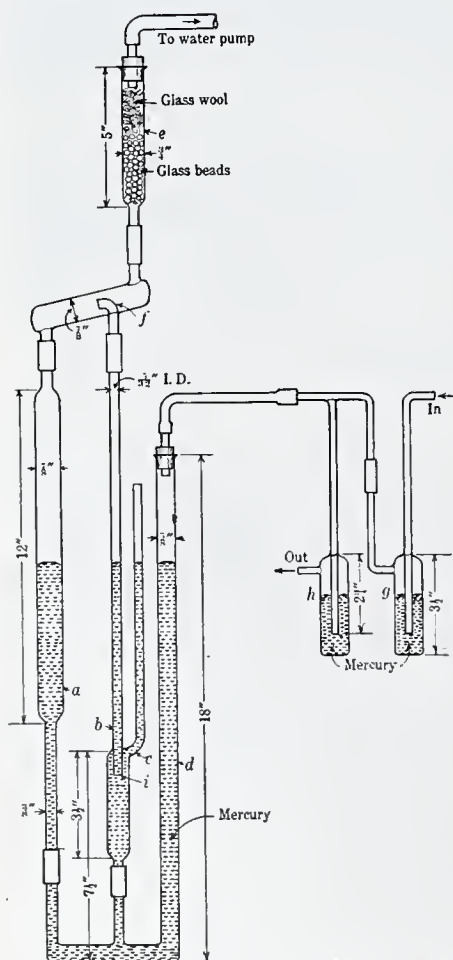


FIGURE 1. PUMP FOR CIRCULATION OF GASES IN CLOSED SYSTEM AGAINST BACK PRESSURE

Ashing Apparatus for Samples Containing Traces of Iodine

GEORGE M. KARNS, Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

IN THE preparation of large samples of organic material for the determination of traces of iodine, recognition of the advantages of ashing samples in systems in which iodine may be recovered from the vaporized combustion products as well as from the ash has led to the development of closed systems for ashing in an atmosphere of oxygen. Most of the devices used for this purpose are based upon the appliance proposed by McClendon (1) and subsequently developed by him and his co-workers.

Although valuable data have been accumulated by the use of apparatus of this well-known type, the operation is often attended with difficulty. With such apparatus it is usually necessary for oxygen to be swept through at a comparatively high rate in order that no loss of products from the sample occurs by expansion during combustion. The rapid rate of this gas stream, from which, of course, the iodine must be recovered, necessitates in turn the employment of a high-capacity washing train involving the use of large amounts of water and reagents which must be eliminated before the final determination is made. Then, too, in apparatus of this type some part of it is subjected to intense heat, either from the burning sample or from external application, and hence its life is short. The apparatus described in this paper has been designed to ash samples slowly if desired. During such slow ashing the oxygen utilization is quite efficient, making it unnecessary to handle a large excess of oxygen and therefore enabling the use of a comparatively simple collecting train. The apparatus is also capable of giving a good ash without the aid of outside heat, and during its operation no destructible part of it becomes so excessively heated as to cause damage.

Figure 1 shows the essential parts of the new apparatus. In carrying out a combustion, the sample is either molded into cylindrical form in a manner similar to that suggested by McClendon and Remington (2), or placed in a paper cylinder fitting the Pyrex glass inner tube *T*. A small amount of suitable fuse material, such as cotton, is put on top of the sample. With the brass ramrod retired, the sample is placed in position, being properly held protruding slightly above the platinum collar, by the stopper and rod. The tube is then set

in position in the bulb and, with the collecting train in place, the desired adjustment of the slight vacuum under which the system is to operate is made, with the oxygen speed regulated to its proper rate. For convenience, the oxygen-inlet tube from a convenient flowmeter is attached at *O*. Carbon dioxide is admitted at *C*, the speed of admission being the minimum of continuous flow through a needle valve. When the system is so arranged, the inner tube is removed from the apparatus, the fuse material is ignited, and the tube is quickly replaced, being held there by rubber bands about the appropriate lugs. As the sample burns, the brass rod is used to push fresh portions of it gently into the flame area, where it is consumed as oxygen becomes available. The globular design of the combustion chamber causes circulating gases to direct the incoming oxygen toward the sample. The rate of burning is adjusted by the oxygen speed. The apparatus illustrated will hold samples of from 35 to 60 grams, depending upon the type of material under consideration. Such sizes of samples are adequate for determinations on most materials, but, if it is desired to analyze large samples, additional cylinders of material may be ashed without interrupting the oxygen flow. When the tube is to be removed to enable the addition of a second portion of sample, the ash may be shaken down into the cup about the central tube, which is provided for that purpose.

As the top portion of the sample burns, radiated heat distills off some of the volatile constituents from lower portions of the sample before it reaches the burning chamber. This distillate is gently swept by the carbon dioxide stream out of the central tube past the platinum collar, which is heated by the burning sample, and through the flame area, where ignition takes place. The carbon dioxide stream also serves to prevent the migration of the flame down into the glass portion of the apparatus, thereby precluding the early destruction of the latter. The combustion products pass into the collecting train through the outlet tube *D*.

The apparatus as illustrated has been used with several sizes of inner tube, but the size shown has been found to be more convenient in general than those of smaller diameter. Little difference in operating the apparatus has been found

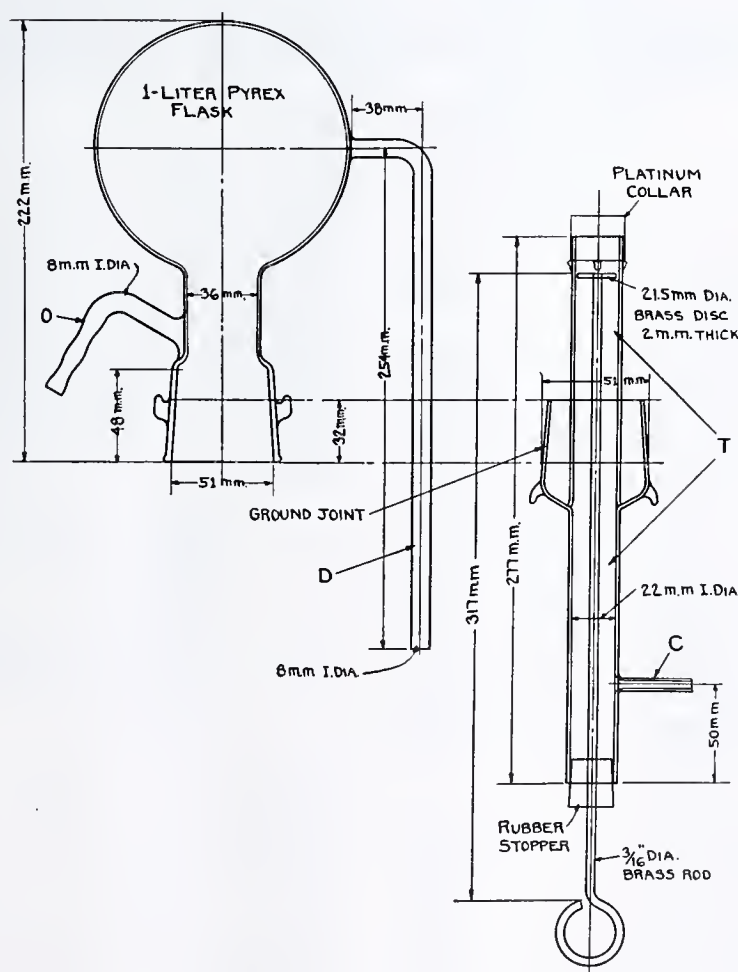


FIGURE 1. ASHING BULB

in working with samples of leafy vegetables, dried milk, mixed cattle foods, tankage, fish scrap, and commercial ground meat. Ground beef containing some fat has been successfully ashed without being previously dried. Using an oxygen speed of 1 liter per minute, a good iodine recovery was made by a simplified collecting train consisting of one condensing tube containing glass wool moistened with sodium bisulfite solution immersed in an ice bath, a Cottrell precipitator 30 cm. in length, and a single Milligan wash bottle containing caustic solution. Operating at the low rate, the average sample is consumed at approximately 25 grams per hour. Although designed to make possible the ashing of samples with a simplified collecting train, the ashing bulb will operate equally well with trains capable of handling the products from a more rapid combustion.

In comparing the apparatus with others previously described, its chief advantage is in its smooth and governable operation. The burning of the sample being complete and controllable, little difficulty is encountered from the development of back pressure from the ignition of accumulated combustibles. It is therefore unnecessary to handle the rapid stream of gas that is usually recommended. It is possible to obtain satisfactory combustion without the usual application of heat from supplementary burners or coils outside or inside the apparatus. Heat-flow direction, distribution, and dissipation make special cooling devices, such as water-circulating coils, unnecessary either in the apparatus or about the feed mechanism. The behavior of the apparatus in this respect also makes it capable of prolonged use when constructed almost entirely of glass.

The above-mentioned features, whose simplicity is readily recognizable by the experienced operator, are difficult to evaluate quantitatively in a procedure which is laborious at

best. However, analysts have developed satisfactory technic using the ashing bulb in four or five trial runs. Since the ashing device is used in the preparation of the sample, recovery is important only as the total procedure is influenced by the device in question. It suffices to say that using the ashing bulb with collecting trains described by McClendon and Remington, the recovery of iodine is equivalent to that obtained by them. When compared with the McClendon and Remington ashing tubes, it is more convenient to clean on account of its size, shape, and lack of internal coils, and on account of the fact that no ash can fuse into the bulb as it sometimes does with glass or silica tubes. The bulbs have been used for approximately one hundred runs without becoming noticeably affected in their hotter portions, a considerably longer life than that of the ashing tube made of Pyrex, which must be used at temperatures approaching its softening point. These, in the hands of operators of some experience, are often in bad condition after five or six runs. The bulb is better in this respect than the more expensive silica tubes, which often crack after alkaline ash fuses into them, even when special precautions are taken.

Experience has demonstrated that the smooth operation of the ashing process in this apparatus makes available dependable types of collection hitherto unutilized in analyzing commodities for iodine.

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RECEIVED December 30, 1931. Presented before the Division of Agricultural and Food Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931.

Determination of Reducing Sugars in Food Products

Proposed Colorimetric Method

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SINCE Lewis and Benedict (4) first announced their colorimetric method for the determination of reducing sugars, several methods have been proposed for the estimation of these sugars in blood and urine. In the field of food chemistry these colorimetric methods have been applied but little.

The authors (7), in testing the effect of some reducing sugars on certain organic nitro compounds, found several compounds which might form a basis for a reagent for the quantitative estimation of reducing sugars in food products. Among these sodium 2,4-dinitrophenolate appeared to be very satisfactory. The purpose of the investigation reported in this paper was to develop a reagent using this compound for the estimation of reducing sugars in food products.

While experimenting with sodium 2,4-dinitrophenolate, many different combinations of this substance with alkalis and alkali carbonates were tried. To the above combinations were added Rochelle salt, phenol, and sodium bisulfite separately and then in various combinations. All of these reagents were tested for the development of color with dextrose. As a result, two different reagents have been sug-

gested, the first to be used when small amounts (1 to 10 per cent) of reducing sugars are present, and the second for larger amounts. Two reagents are suggested in order that the dilution factor may be eliminated as far as possible with the foods containing a large percentage of reducing sugars:

1.	Sodium 2,4-dinitrophenolate	8 grams
	Sodium hydroxide, 5 per cent	200 cc.
	Phenol	2.5 grams
	Rochelle salt	100 grams
	Distilled water, q. s.	1000 cc.
2.	Sodium 2,4-dinitrophenolate	8 grams
	Sodium hydroxide, 5 per cent	200 cc.
	Rochelle salt	100 grams
	Distilled water, q. s.	1000 cc.

In the above formulas the sodium 2,4-dinitrophenolate and phenol are dissolved in the sodium hydroxide solution. The Rochelle salt is dissolved in about 700 cc. of water. The solutions are mixed and diluted to 1 liter.

The procedure used for the estimation of the reducing sugars may be stated as follows: A given amount of the food product containing the reducing sugars is weighed and the necessary dilution made. One cubic centimeter of this dilution

is placed in a Folin-Wu sugar tube, and 3 cc. of the proper reagent (depending upon the amount of reducing sugar present) are added. The tube is heated in a beaker of boiling water for 6 minutes, then cooled in running water for 3 minutes, and finally diluted to the 25-cc. mark with cold distilled water. Then this solution is compared in a colorimeter with a standard made by treating a given amount of pure glucose in the same manner as the unknown. The side of the colorimeter containing the unknown is set at 20, and the standard varied until the colors match. An average of five readings is taken and the percentage of the reducing sugars calculated.

TABLE I. READINGS FOR 1 PER CENT GLUCOSE IN SOLUTION WITH DIFFERENT AMOUNTS OF SUCROSE

(Per cent sucrose)								
At 0	At 5	At 10	At 20	At 30	At 40	At 50	At 60	At 70
20.0	20.2	19.8	20.0	20.0	20.0	20.0	19.8	20.0
20.2	19.8	20.2	19.8	20.2	19.8	19.8	19.8	20.2
20.3	19.9	20.0	20.1	20.1	20.2	20.0	20.0	20.0
19.8	20.0	20.0	20.0	20.0	19.8	20.0	20.0	19.8
19.9	20.1	20.2	19.8	20.0	19.9	20.2	20.0	20.0
Av. 20.04	20.00	20.04	19.94	20.06	19.94	20.00	19.92	20.00

With the ordinary sirups, jellies, jams, and fruit juices, the color present did not interfere with the accuracy of the method. In products very high in coloring matter, such as molasses, preliminary clarification was necessary. The use of neutral lead acetate as directed in the Methods of Analysis of the Association of Official Agricultural Chemists (6) was satisfactory. This clarification could also be accomplished with alumina cream, fuller's earth, decolorizing carbons, and dry basic lead acetate without interfering with the accuracy of the method.

Because of the fact that the percentage of reducing sugars in the original food product is not known, readings are often obtained which are not very close to the standard reading of 20. This brought up the question as to whether or not the colorimetric method was accurate when these readings were rather far apart. Solutions were prepared containing glucose in varying amounts from 0.5 to 3 per cent. The color developed by these amounts was compared to a solution containing 1 per cent glucose. In each case, the correct theoretical readings were obtained. These experiments showed that with the proposed reagents, the intensity of the color is directly proportional to the amount of glucose present. This is a distinct advantage, because it is difficult to have the standard and unknown always read exactly the same. According to Rothberg and Evans (8), this is not true for the Folin and Wu method; and Folin and Denis (3) and Bierman and Doan (2) state this is also the case with the picric acid method. Sumner (9), however, found with his method that 1 mg. of glucose compared to 0.5 to 2 mg. of glucose without error. Benedict (1) made the same observations with his method.

Many food products contain a large amount of sucrose and a small amount of reducing sugars. Therefore, a series of experiments was conducted to determine whether or not a large amount of sucrose had any effect on the accurate estimation of the reducing sugars by the proposed method. Solutions were prepared containing 1 per cent of glucose with varying amounts of pure sucrose—namely, 10, 20, 30, 40, 50, 60, and 70 per cent. A determination was made of each of these solutions by comparing the color developed with a 1 per cent solution of pure glucose as the standard. Table I gives the reading found in these determinations when the standard was set at 20.0.

As may be seen from the average reading given in Table I, the different amounts of sucrose had no effect on the accuracy of the determination of glucose by the proposed method.

Since reducing sugars in food products usually contain levulose, the reducing equivalent was determined for this sugar. With the proposed method, it was found to have exactly the same reducing power as dextrose.

Frequently, when colors are developed by reducing sugars in alkaline solutions of organic nitro compounds, their intensities are either changed according to the length of the time of heating, or fade upon standing. Eight tubes, each containing the same amount of glucose, were heated with the reagents for varying lengths of time—namely, 5, 7, 10, 12, 15, 20, and 25 minutes. The results indicated that the time of heating up to 25 minutes caused no difference in the color produced. Subsequent work has shown in every case that 6 minutes is ample time for complete reduction to take place. Similar experiments were conducted differing only in that the various tubes, after having been heated for 6 minutes, were allowed to stand from 5 to 20 minutes immediately after the dilution of their contents. No change in the color was noted up to 20 minutes' standing.

The proposed colorimetric method was used to determine the reducing sugar in a number of food products. Table II gives the results for pure maple sirups, cane and maple sirups, and maple sugars. Table III includes the results when fruit juices, jams, and jellies were analyzed. Table IV gives the results of the analysis of milk for lactose. In all of the food products, the reducing sugar was also estimated by the official Munson and Walker method (5).

TABLE II. ANALYSIS OF SIRUPS AND MAPLE SUGAR FOR REDUCING SUGARS

FOOD PRODUCT	AUTHORS' METHOD	MUNSON-WALKER METHOD
	%	%
Pure maple sirup	6.23	6.08
Pure maple sirup	3.40	3.24
Pure maple sirup	1.83	1.94
Pure maple sirup	6.62	6.58
Pure maple sirup	2.56	2.48
Pure maple sirup	2.29	2.22
Cane and maple sirup	2.22	2.03
Cane and maple sirup	1.66	1.61
Cane and maple sirup	2.20	2.12
Cane and maple sirup	4.82	4.65
Cane and maple sirup	2.29	2.22
Cane and maple sirup	1.16	1.05
Beet molasses sirup	0.52	0.61
Cane sugar sirup	1.42	1.31
Beet sugar sirup	1.22	1.21
Maple sugar	6.50	6.49
Maple sugar	5.68	5.60
Maple sugar	5.66	5.72
Cane and maple sugar	0.95	0.83

TABLE III. ANALYSIS OF FRUIT PRODUCTS FOR REDUCING SUGARS

FOOD PRODUCT	AUTHORS' METHOD	MUNSON-WALKER METHOD
	%	%
Apple juice	9.60	9.54
White grape juice	13.45	13.39
Pineapple juice	9.00	8.91
Orange juice	5.03	5.10
Loganberry juice	9.05	8.92
Grapefruit juice	30.87	30.92
Apple jelly	16.45	16.61
Grape jelly	23.81	23.92
Raspberry jelly	16.96	17.12
Currant jelly	48.78	48.92
Plum jam	48.80	48.90
Strawberry jam	48.88	48.81

TABLE IV. ANALYSIS OF MILK FOR LACTOSE

MILK	AUTHORS' METHOD	MUNSON-WALKER METHOD
	%	%
Raw	4.63	4.60
Raw	4.80	4.74
Pasteurized	4.35	4.29
Pasteurized	4.73	4.68

From Tables II, III, and IV, we see that the proposed method checks very closely with the Munson and Walker method. The latter, however, in some cases gives slightly lower results, but the proposed method has the advantage

over the Munson and Walker method in that it is much more rapid.

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RECEIVED January 22, 1932.

Measurement of Surface Hardness of Cellulose Derivatives

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FOR many purposes the surface hardness, including resistance to abrasion and indentation, of films and plastics formed from cellulose derivatives is of equal importance with the mechanical strength of the material in the mass. Various methods of measuring the hardness and resistance to abrasion have been suggested at one time or another. In this laboratory there has been developed and used for some time a method of measuring the resistance to scratching which gives quantitative results and which seems of interest as furnishing another criterion of the physical properties of cellulose derivatives.

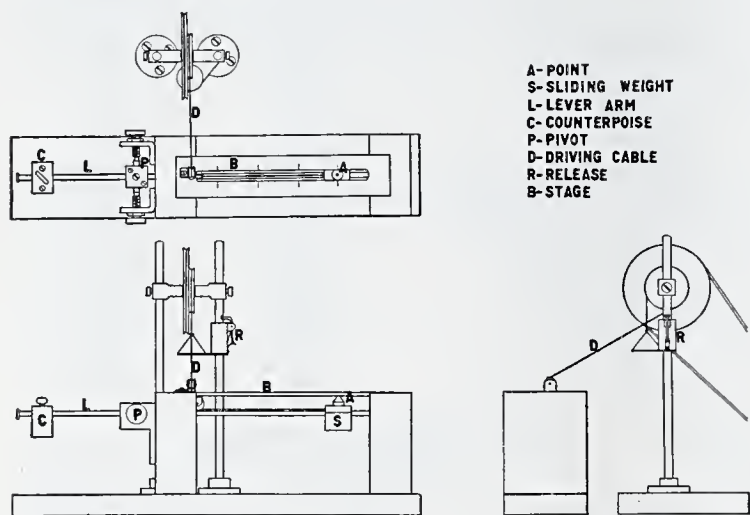


FIGURE 1. DIAGRAM OF SCRATCH DYNAMOMETER

The comparison of the findings obtained by this apparatus with the results of direct abrasion tests comes properly under the subject of testing materials, particularly the testing of paints, lacquers, and varnishes, and this phase of the work will be discussed in another place.

APPARATUS AND METHODS OF MEASUREMENT

The apparatus used consists essentially of two instruments. One of these is a scratch dynamometer and the other a scratch-observing instrument. Scratch dynamometers may be divided into two types: (1) a series of scratches is produced, each made with a constant load, the load increasing from one scratch to another; (2) a single scratch is made under a load increasing at a definite rate. Instruments have been designed for both purposes, but most of the work described here was carried out with an instrument of the second type, whose construction is shown in Figure 1.

The apparatus is devised to produce a scratch by a

moving point starting from zero load, the load increasing steadily up to the desired limit. In the operation of the scratch dynamometer, the sample is placed in the holder at A so that the face is parallel to the base and turned downward. The material is best used in the form of thin, uniform films coated on glass although, where desired, coatings may be on metals or other rigid supports, or skived plaques of sufficient rigidity may be taken. Point A is fitted on a slide weight, S, which is drawn from its initial position of zero load (in counterpoise) by the weight C back toward a pivot, P. Traction is effected by the cable D running over a pulley driven by a constant-speed motor. Movement is started by the release R, and a scratch is produced by the point operated under a load increasing according to the equation: $L = \frac{d.W}{b-d}$

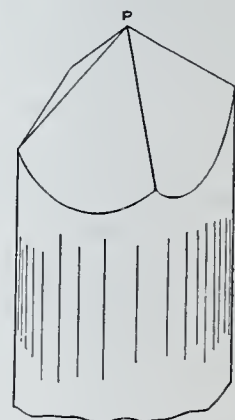


FIGURE 2. SHAPE OF POINTS

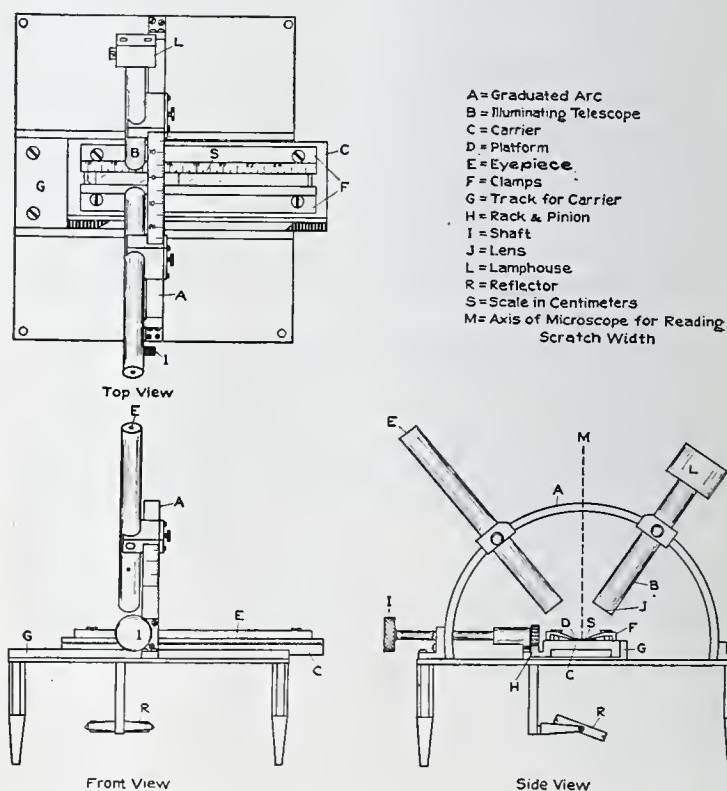


FIGURE 3. DIAGRAM OF ILLUMINATOR FOR SCRATCH TESTER

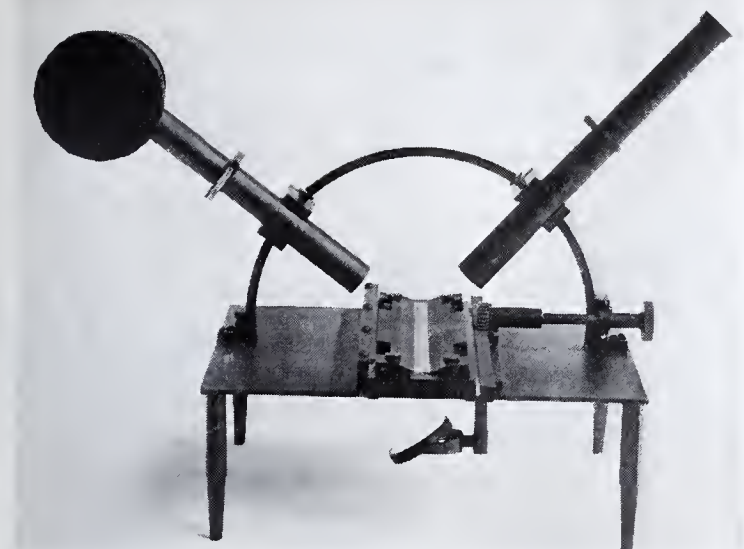


FIGURE 4. ILLUMINATOR FOR SCRATCH TESTER

where L = load on point
 W = weight of S
 b = original distance of point from pivot
 d = distance traveled by point

Thus in a specific instance,

$$W = 145 \text{ grams}$$

$$b = 25 \text{ cm.}$$

hence
$$L = \frac{145 d}{25 - d} \text{ grams}$$

A straight scratch ready for examination in the illuminator is produced.

The type of scratch and the scratch susceptibility depend on the kind of point chosen. Not only will the material of the point affect the results, but also the shape of the point or style. In the experiments described, a hardened steel point shaped to an inverted tetrahedron of 45 degrees was used (Figure 2).

OBSERVATION AND MEASUREMENT OF SCRATCH SUSCEPTIBILITY

Measurement of scratch susceptibility may be expressed either as the threshold load just producing a scratch, or by a curve expressing the relation between the magnitude of the scratch and the load.

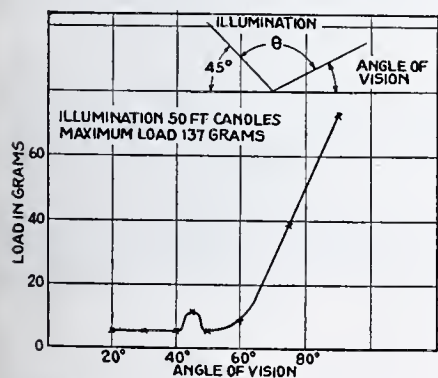


FIGURE 6. THRESHOLD VALUE AS FUNCTION OF ANGLE OF VISION

The illuminating tube, L , and the observing tube, E , are movable on a graduated circle, A , the scratch being on a line passing through the center of the circle and perpendicular to its plane. The appearance of the scratch at any point along its length can be examined, the scratch being moved forward by a rack and pinion at H and I . The carriage is graduated as shown at

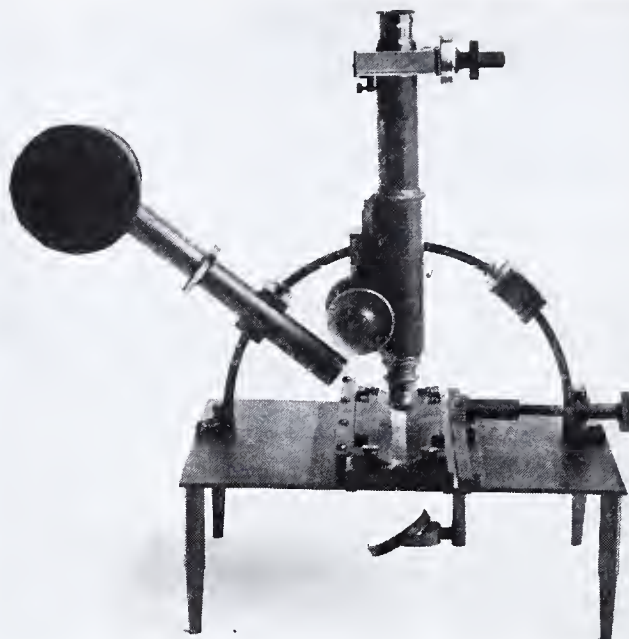


FIGURE 5. ILLUMINATOR IN POSITION FOR SCRATCH-WIDTH MEASUREMENT

S , the graduations corresponding to different loads, according to the equation already given. The illuminator, L , is adjusted to give a constant level of illumination, and the scratch may be examined either by reflected light or by light transmitted by the mirror, R .

The least load making a perceptible scratch will depend upon the visibility conditions, and therefore upon the amount and angle of illumination. The scratch illuminator is operated in a dark room or dark cabinet. Experimentally it was found that an angle of approximately 30 degrees was most satisfactory, avoiding both specular reflection and grazing incidence of the light. It will be seen from the curves

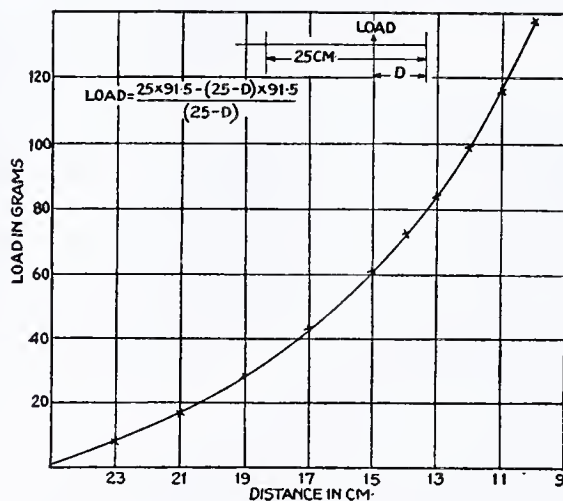


FIGURE 7. SCRATCH-LOAD CALIBRATION CURVE

in Figure 6 that the angle chosen is in a flat portion of what may be termed the "angular visibility" curve, and the glare and reflected image which occur at specular reflection at 40 degrees are avoided. In Figure 7 is given a scratch-load calibration curve, by which intervals along the scratch are converted to effective loads. The illumination level at the scratch used in the present work was 50 foot-candles, corresponding to an average indoor illumination.

SCRATCH-WIDTH MEASUREMENTS. The magnitude of the scratch is best determined by measurements of the width of the scratch at a given load. To measure this, a microscope is mounted on the graduated circle, A , carrying a filar eyepiece micrometer. The arrangement of this is shown in

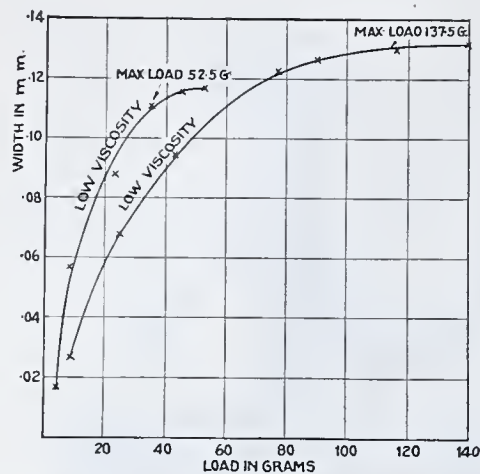


FIGURE 8. CHARACTERISTIC SCRATCH-WIDTH CURVES FOR NITROCELLULOSE

frequently of value to get an idea of the qualitative character of the scratch, such as tendency to splinter along the furrow, to give a ragged, rough, or smooth furrow, etc. The appearance can, of course, be noticed during the scratch-width measurement, but a permanent record can be obtained by substituting a small camera for the eyepiece micrometer and taking a photograph at low magnification.

EXPERIMENTAL RESULTS

The experimental data presented at this time are given by way of illustration. In Figure 8 are given curves of scratch-width, illustrating the behavior of a low-viscosity nitro-cotton film. It can be seen that the scratch seems to start from finite value of the load, which would be practically identical with what has been termed the "scratch suscepti-

bility." When the width of the scratch produced at each load is measured, this can be plotted as a function of the scratch load. There is thus obtained a characteristic abrasion curve for the surface in question under the given point.

APPEARANCE AND QUALITY OF SCRATCH.

The effect of some so-called plasticizers upon the scratch susceptibility is shown in Table I.

TABLE I. EFFECT OF PLASTICIZERS
(Low-viscosity nitrocellulose (half-second), 100 parts)

PLASTICIZER	AMOUNT %	THRESHOLD VALUE	
		Max. load, 52.5 grams	Max. load, 137.5 grams
		Grams	Grams
Camphor	60	17	21
Triphenylphosphate	60	4	9
Tri- <i>o</i> -cresylphosphate	60	25	32
Ethyl phthalate	60	34	41
		35	47

This shows the distinctly characteristic effect of camphor with nitrocellulose, compared with other so-called plasticizers. To compare these values with other surfaces, the following values may be cited:

SUBSTANCE	THRESHOLD VALUE	
	Max. load, 52.5 grams	Max. load, 137.5 grams
	Grams	Grams
Nitrocellulose (low viscosity)	17	21
Nitrocellulose (high viscosity)	14	20
Spar varnish	32	28

The characteristic action of plasticizers actually requires measurement at different proportions, giving a characteristic curve for each plasticizer.

ACKNOWLEDGMENT

Thanks are due G. Willis, formerly of these laboratories, who helped materially in the construction of the dynamometer.

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Determination of Melting Points of Special Waxes

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IN THE course of some work on determining the melting points of special waxes, it was noticed that the standard methods—i. e., the drop method, wherein the thermometer bulb is given a thin coating of the wax whose melting point is to be determined, and the capillary tube method, wherein the finely powdered wax is shaken into the tube—were inaccurate. The chief difficulty encountered was that these waxes have the property of becoming transparent and gelatinous at a point varying from 18° to 35° C. below their melting points.

In the case of the capillary tube method, the softening point could not be distinguished from the melting point. In the case of the drop method, the melting and softening points were more easily distinguishable. Nevertheless, neither of the methods was adequate, and, therefore, a method which is applicable to these special waxes and also to other waxes was worked out.

Fill a 4-inch (10.16-cm.) length of 0.25-inch (0.62-cm.) tubing having a 3/16-inch (0.58-cm.) bore to a depth of 2 inches (5.08 cm.) with the wax by sucking it up into the tube while molten. Hold the thumb over the unfilled end of the tube and blow on the filled end until the wax has cooled sufficiently to retain its position in the tube. Then lay it down and allow to remain for a half hour to cool to room temperature, leaving it open at both ends. Fasten it to a thermometer so that the upper level of the wax is on a level with the water in the beaker. Raise the temperature at the rate of about 3° C. per minute, and make readings as follows:

- 1. Softening point = temperature at which wax becomes transparent.
- 2. Melting point = point at which mass first starts to rise in tube.

Taking Table I as a basis for comparison, in which tests were made on three samples of special waxes and three other standard waxes, the results obtained by all three methods show that:

- 1. Softening points can be determined in all cases by the float method.
- 2. Melting points can be determined in all cases by the float method, whereas they cannot be determined accurately by the capillary tube method.
- 3. Melting points can be determined with greater accuracy by the float method than by the other two methods.
- 4. The float method is more accurate for the determination of the melting point because the melting point is taken at an exact point rather than at a range of several degrees.

TABLE I. RESULTS OF TESTS						
WAX	DROP METHOD		CAPILLARY TUBE		FLOAT TEST	
	S. P.	M. P.	S. P.	M. P.	S. P.	M. P.
	° C.	° C.	° C.	° C.	° C.	° C.
I. Paraffin	...	56-58	..	54-56	..	56
II. Carnauba wax	...	85-87	..	84-86	..	86
III. Carnauba wax, refined	...	84-86	..	83-85	..	86
IV. Gelowax 1	60	78	?	56-58	59	78
V. Gelowax 2	60	95	?	55-57	60	95
VI. Gelowax 3	56-60	79-87	?	56	60	90

S. P. = softening point; M. P. = melting point.

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Determination of Total Solid Matter and Density of Egg White by Refractometer

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DURING investigations dealing with the deterioration of eggs it became desirable to have a rapid method for estimating the total solid matter in natural egg white. It was found possible to use the index of refraction, obtained with a common type of refractometer, as a measure

the two methods was found to be satisfactory. Specific gravities of the egg white samples were determined by a specific gravity balance at 25° C.

The sum of the protein and mineral components has been plotted, as per cent total solids, against the index of refraction.

The relationship appears to be linear, as is also true for the relationship between specific gravity and index of refraction. To enable reconstruction of the graphs, the following points, taken accurately from the plots, are given:

INDEX OF REFRACTION	TOTAL SOLIDS	SPECIFIC GRAVITY
n_D^{25}	%	d_{25}^{25}
1.3520	10.55	1.0312
1.3600	14.55	1.0442

Egg white may be considered to be protein, mineral, and water only, the mineral component of the white being a small and nearly constant fraction of the total (the ash obtained from the white amounted to 0.80 per cent on the average). For this reason the system behaves as a binary mixture. A linear variation such as that found is required by the Lorenz-Lorentz formula (1) for the specific refraction of binary mixtures where partial molal volumes may be considered constant.

Although the figures and data suggest that both the index of refraction and the

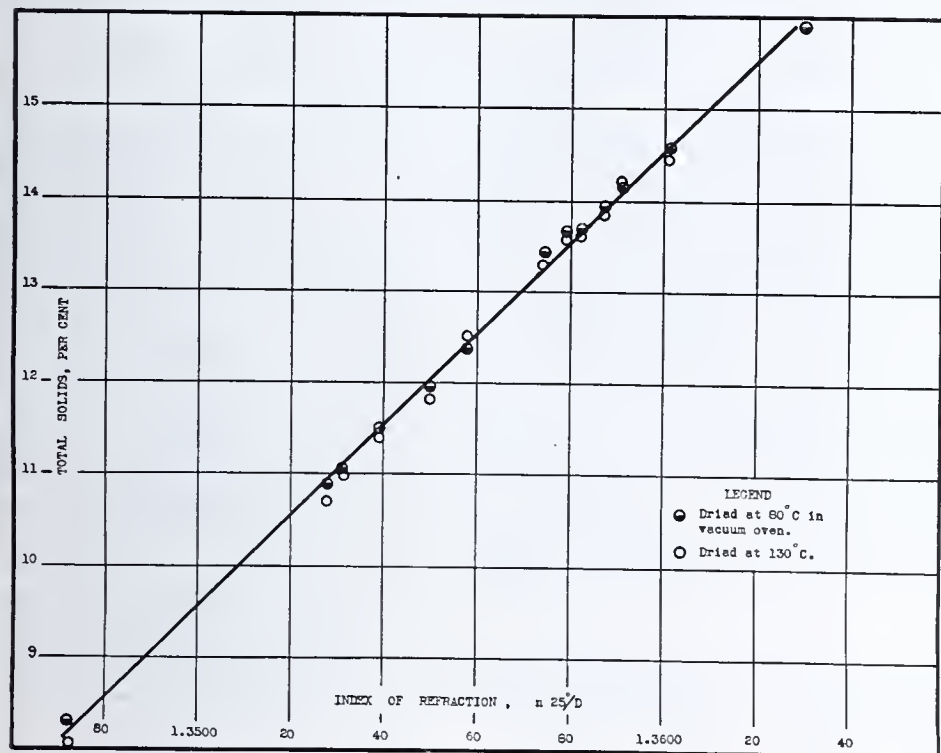


FIGURE 1. RELATIONSHIP OF TOTAL SOLIDS, DETERMINED BY TWO METHODS, TO INDEX OF REFRACTION IN NATURAL EGG WHITE

of this solid matter. Since many agricultural research stations about the country are engaged in studies of egg problems, it appeared that the method to be described might be of general interest and value.

In a previous paper from this laboratory (2) the use of the refractometer in studying the distribution of total solids between firm and liquid white has been described. This work has been repeated and extended over a greater range in so far as the relationship between refractive index and total solids is concerned. In addition, the densities of the samples of white were obtained.

The refractive index was measured at 25° C. with a Spencer refractometer, Abbé type. This may be done in a few seconds. The total solid matter in the samples of egg white was found in two ways—by drying in an oven at 130° C. and one atmosphere, and by drying at 80° C. under a vacuum of 29 inches of mercury. In each case the drying was continued until successive weighings showed a negligible decrease in weight. The agreement between

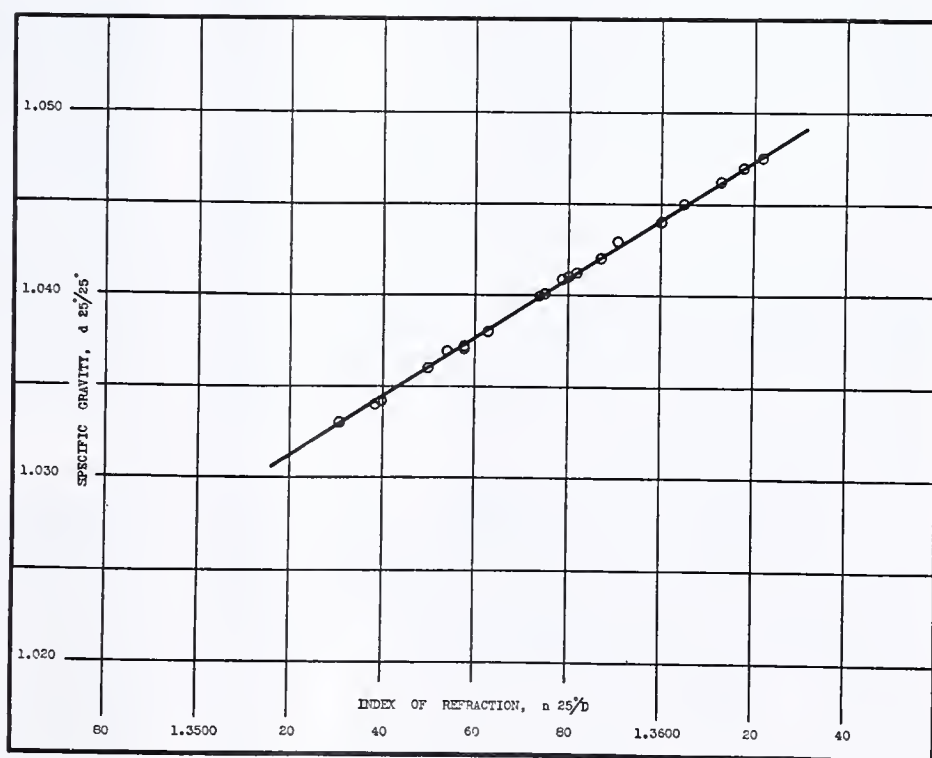


FIGURE 2. RELATIONSHIP OF SPECIFIC GRAVITY TO INDEX OF REFRACTION IN NATURAL EGG WHITE

specific gravity may serve with nearly equal accuracy as a measure of the total solids content, the use of the former proves much more convenient, as it may be determined with greater ease and speed and with only a drop or two of the sample. In conclusion, we wish to point out that it is fundamentally unsound to apply this method to a study of egg yolk or whole egg, since these mixtures contain more than two major components. This condition makes possible an

indefinite series of mixtures all of which may have the same refractive index.

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Rapid Method for Determination of Boron

Suggested Procedure for Evaluation of Boron-Bearing Ores for Boron Content

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SOME years ago the senior author published a method for the evaluation of boron-bearing ores in his work on "Standard Methods of Chemical Analysis." The procedure followed the generally accepted principles for the evaluation of boronatrocalcite, borocalcite, boracite, and boron-bearing ores decomposed by hydrochloric acid, but was not adapted to higher grades of ore now found in California, or to concentrates. Considerable contrary opinions exist on the details for an exact and rapid method for the commercial evaluation of these ores, which induced one of the large shippers of the ore and ore concentrates to request the senior author to investigate the existing procedures more generally accepted as standards. The matter being of personal interest, the senior author undertook the work and carried out a series of tests in his laboratory at the University of Southern California and worked out details of the method recommended in this paper. The general procedure was tested by colleagues—Arthur Zeisner, Russell G. Dressler, H. W. Olson, and L. K. Gates—and certain modifications were made in the original method. Valuable information was obtained from commercial laboratories. We would mention specially A. R. Maas, Maas Chemical Laboratory, Los Angeles; George A. Connell and K. Jacoby, Pacific Coast Borax Company, Los Angeles; George Tate, Analytical Laboratory, Liverpool, England; Dr. C. Ahrens and Dr. Ad. Gilbert, Offentliches Chemisches Laboratorium, Hamburg, Germany; H. L. Payne, Baverstock and Payne, Los Angeles; A. Osgyani, Raymond G. Osborne Laboratory, Los Angeles; Smith-Emery Company, Los Angeles; and Dr. K. J. Suckow, Suckow Borax Mines, Calif.

The presence of iron and aluminum in the ores necessitates their removal from the solution titrated for boric acid, since these would also titrate and lead to high results. Provision is generally made for their removal in the accepted methods, but little attention is given to the recovery of occluded boric acid carried out by the precipitates. Wherry and Chapin (2) recommend the precipitation of the boric oxide group by addition of calcium carbonate; Connell and Jacoby use barium carbonate; Gilbert and Tate suggest the use of sodium carbonate. Ammonium hydroxide, magnesium carbonate or oxide, and sodium hydroxide have been used.

By using sodium hydroxide to precipitate the iron and aluminum in boric acid solutions quantitatively, when using sofrol red or p-nitrophenol indicator, at least 30 minutes are saved over the method of using sodium carbonate. The results of approximately one hundred and fifty determinations show that the method gives very satisfactory results. The end points are good. The error in all the determinations has not been greater than 0.25 per cent. The method is applicable to commercial boron-bearing ores such as crude borax, kernite, tincalconite, ulexite, colemanite, and boracite.

The senior author finds that the use of ammonia, with the resulting formation of ammonium chloride, leads to high results and an uncertain end point in the titration; and also that in the presence of free boric acid aluminum may be precipitated by addition of sodium hydroxide completely, without formation of the soluble sodium aluminate, at the stage when approximately one-third of the free boric acid is neutralized. A suitable indicator is used to ascertain the end point of subsequent neutralization, before addition of the polyhydric alcohol. A method for the recovery of occluded boric acid has been investigated.

RECOVERY OF OCCLUDED BORIC ACID

EFFECT OF IRON AND ALUMINUM SALTS. A positive error resulted in direct proportion to the amount of salts present. For example, 1 gram of aluminum chloride (aqua) added required an additional titration of 25.3 ml. of 0.552 *N* sodium hydroxide.

OCCLUSION OF BORIC ACID BY IRON AND ALUMINUM PRECIPITATES. In a sample of "tincal" containing 1.9 per cent of iron and aluminum oxides and over 44 per cent of boric oxide, a loss of 1.15 per cent of boric oxide occurred by occlusion of the boric acid by the iron and aluminum hydroxides precipitated, by sodium carbonate solution washed six times; and 1.53 per cent by the precipitate washed twice. It was found that 0.2355 gram of aluminum hydroxide held 0.1922 gram of boric oxide, washed twice. Further results appear later.

GAIN OF MOISTURE IN BORATE CONCENTRATES. The necessity of keeping the representative sample in a closed container is shown by the following tests: A 5-gram sample taken from material as received was exposed to the air for 1 hour. In this time the sample gained 24.5 mg. of moisture. In 2.5 hours it had gained 66.1 mg., or over 1 per cent.

WATER DISPLACEMENT OF CLAY RESIDUE. In rapid methods where the clay is allowed to settle and the solution is made to definite volume, an allowance is made for the volume occupied by the residue in the flask. The senior author found that 10.08 grams of this residue in the analysis

of "tincal" occupied a space of 4.8 ml., or approximately 0.5 ml. per gram of residue.

PRECIPITATION OF ALUMINUM HYDROXIDE BY SODIUM HYDROXIDE IN PRESENCE OF FREE BORIC ACID. The sample from the acid extraction of the borate concentrate was titrated in the presence of phenolphthalein indicator to a faint pink color (the polyhydric alcohol being omitted), aluminum hydroxide was completely precipitated, and no evidence of sodium aluminate in the filtrate was obtained. It was found that approximately one-third of the boric acid in the solution was neutralized at this stage, and the free boric acid evidently prevented the formation of the soluble sodium aluminate.

RAPID METHOD VS. CHAPIN'S DISTILLATION METHOD. Some doubt has been expressed regarding direct titration methods by the customary procedure. It is felt that the isolation of boric acid from interfering elements is necessary for accurate results. Any one who is familiar with the distillation method realizes the disadvantages of this long procedure in the evaluation of boron-bearing ores and the danger of error due to factors in the procedure and the small amounts of boron that can be determined. The comparisons given in Table I, however, are of value and interest. Better checks with the Chapin method are obtained by using mannitol and titration in the presence of sofnol indicator.

TABLE I. DIRECT TITRATION METHOD VS. CHAPIN'S DISTILLATION METHOD^a

CHAPIN'S Gram	DIRECT TITRATION Gram
BORIC OXIDE, 0.5-GRAM SAMPLE ^b	
0.2195	0.2221
0.2189	0.2228
0.2199	0.2213
PURE BORIC ACID, 0.1-GRAM SAMPLE	
With glycerol and <i>p</i> -nitrophenol indicator	
0.0972	0.1012
0.0966	0.1011
0.0967	0.1011
With mannitol and sofnol indicator	
	0.0996
	0.0996 +
	0.1005
	0.1002

^a Data by H. W. Olson.

^b In Chapin's method, 0.5 gram of ore; in direct titration method, aliquot portion of sample equivalent to 0.5 gram.

The results of tests reported in Table II show the degree of precision in checks that can be expected by direct titration of the solution containing the borate.

TABLE II. COMPARISON OF RESULTS OF DIRECT TITRATION OF SOLUTION CONTAINING BORATE

CRUDE CRUSHED ORE 30-gram sample %	COARSE DUMPLINGS 10-gram sample %	FINE DUMPLINGS 10-gram sample %	CONCENTRATE 10-gram sample %	CONCENTRATE AT MINE 10-gram sample %
25.00	13.40	28.28	44.30 ^a	48.20
25.52	13.45	28.80	44.12	48.38
			44.10	
			44.38	
			44.42 ^b	
			44.54	
			44.25	

^a Data by Russell G. Dressler.

^b Data by H. W. Olson.

OCCCLUSION OF BORIC ACID. In studying the occlusion of boric acid by aluminum hydroxide when precipitated with sodium hydroxide, which has been mentioned, it was found that definite amounts of the acid are occluded. The amount depends on the concentration of the solution and the per cent of aluminum present. From the data in Table III it will be seen that if the amount of aluminum present is less than 0.2 per cent, the occluded boric acid need not be run when the concentration of the sodium hydroxide reagent is above 0.5 normality.

TABLE III. OCCCLUSION OF BORIC ACID BY ALUMINUM HYDROXIDE^a

(0.6184-gram sample taken)

SAMPLE	ALUMINUM ADDED %	H ₂ BO ₃ OBTAINED %	H ₂ BO ₃ OCCLUDED %	AVERAGE H ₂ BO ₃ OCCLUDED %
1	None	100.00 ^b	0.00	0.00
2	None	100.00 ^b	0.00	
3	0.2	99.75	0.25	0.25
4	0.2	99.75	0.25	
5	0.5	99.25	0.75	0.62
6	0.5	99.50	0.50	
7	1.0	98.55	1.45	1.45
8	1.0	98.55	1.45	
9	2.0	97.34	2.66	2.78
10	2.0	97.10	2.90	

^a Data by Arthur Zeisner.

^b Standard solution.

In the analysis of ten synthetic samples, including two blanks, the occluded boric acid was recovered and the amount added for total percentage of boric acid. A maximum error of 0.25 per cent was obtained. Since aluminum hydroxide is a gelatinous substance, the amount present in a sample will determine the length of time required in filtering the solution in order to obtain all of the occluded boric acid.

The following report of analysis of a California concentrate received at Liverpool, England, was received from the George Tate Laboratory:

	SCOTT'S METHOD	METHOD BY TATE
Lot A, % B ₂ O ₃	42.40	42.50
Lot B, % B ₂ O ₃	42.50	42.25

An excess of acid used in the original digestion of the ore has practically no effect on results, this excess being taken care of in the procedure. The following results from the Raymond G. Osborne Laboratory supports the statement. Ten-gram samples were examined.

AMT. OF N HCl Cc.	BORIC OXIDE %
50	43.94
75	44.15
100	44.15

WATER-SOLUBLE BORATES. It may be desired to evaluate the ore by determining its water-soluble content. The California deposits of sodium borates are largely water-soluble. The residue must be examined also if total borate is desired. The water extraction is made in a covered beaker, the reflux condenser being unnecessary.¹ The following report was obtained from a local commercial laboratory.

	SCOTT'S METHOD		GILBERT'S METHOD		OSBORNE'S METHOD	
	A	B	A	B	A	B
	%	%	%	%	%	%
Water-soluble B ₂ O ₃	46.35	46.24
B ₂ O ₃ in residue	1.32	1.65
Total B ₂ O ₃	47.70	47.89	48.04	48.08	48.05	47.84

DETERMINATION OF TOTAL ACID-SOLUBLE BORATE

The finely ground ore is boiled with hydrochloric acid in a flask connected to a reflux condenser. The solution is made up to a definite volume and portions of the filtrate taken for analysis. The iron and aluminum are first precipitated quantitatively with sodium hydroxide using *p*-nitrophenol as the indicator. The iron and aluminum hydroxide precipitate is filtered off, and the boric acid is titrated with standard sodium hydroxide in the presence of glycerol, using phenolphthalein as the indicator. The iron and aluminum hydroxides are redissolved in 6 *N* hydrochloric acid and then reprecipitated with sodium hydroxide added very cautiously, and filtered to separate the occluded boric acid. The solution from the iron and alumina is now titrated with sodium hydroxide as above.

¹ Even in the presence of acid practically no loss of boron occurs at temperatures just below boiling. This confirms the results of Dodd and Scott (1).

ACID EXTRACTION. The method is applicable for the determination of total boric acid in borates of sodium, calcium, and magnesium in materials such as crude borax, tincalconite, kernite, boracite, ulexite, colemanite, etc. Silicoborates required a preliminary fusion with sodium carbonate. The acid residue should be examined for these. Iron, aluminum, ammonium salts, and substances other than boric acid should be absent from the solution if they react with sodium hydroxide.

REAGENTS

1 or 0.5 *N* HCl
 1 or 0.5 *N* NaOH (carbonate-free)
 6 *N* HCl (acid of constant boiling point is satisfactory)
 50% solution of NaOH (carbonate-free)
 Indicators: *p*-Nitrophenol (saturated water solution)
 Sofnol red No. 1
 Phenolphthalein (1% in 50% alcohol solution)
 Mannitol or glycerol
 Water, carbon dioxide-free

A five-gram sample, finely ground, is placed in a 250-cc. volumetric flask, 15 to 20 cc. of 6 *N* hydrochloric acid are added, together with an equal volume of water, and the flask connected to a reflux condenser. The mixture is heated to boiling and boiled for 20 to 25 minutes. After allowing to cool slightly, 75 cc. of water are poured into the flask through the condenser tube, the solution mixed, and then the heating and boiling repeated for 10 to 15 minutes. The flask is again allowed to cool slightly and about 50 cc. of water poured through the condenser tube into the flask. The condenser is disconnected, and the flask placed in a cold water bath and cooled.² Water is now added to the 250-cc. mark, and if necessary an additional amount to allow for the volume occupied by the residue.³ After the residue has settled, the clear solution in the quantity desired is decanted through a dry filter into a dry, clean beaker, and portions of this filtrate taken for analysis. Fifty cubic centimeters are equivalent to 1 gram of the original sample.

Of the filtrate, 50 or 100 cc. are taken, according to the strength of the reagents used, and placed in 400-cc. beakers.

REMOVAL OF IRON AND ALUMINUM. To the boric acid solution in a beaker are added 3 to 4 drops of sofno red or *p*-nitrophenol indicator. Standard sodium hydroxide is added cautiously until the yellow color of the indicator remains. All the iron and aluminum will be precipitated at this point. The solution is heated gently, then allowed to stand for several minutes. The iron and aluminum hydroxide are filtered off and washed with hot water, and the filtrate and washings titrated for boric acid according to the procedure given under titration of boric acid below.

RECOVERY OF OCCLUDED BORIC ACID. The iron and aluminum hydroxide carry out very appreciable quantities of boric acid when precipitated in the presence of a large excess of this acid. If the amount of these hydroxides is appreciable, the recovery of boric acid is essential for accurate results.

The hydroxides are dissolved in the filter by addition of 6 *N* hydrochloric acid, added in sufficient excess. The acid solution is caught in a beaker together with hot washing of the filter. Three to four drops of sofno red or *p*-nitrophenol are added to the solution, and sodium hydroxide (50 per cent solution) is now added dropwise until about neutral, then 0.5 *N* sodium hydroxide until the yellow color of the indicator remains. The solution is heated gently, then allowed to stand for several minutes. The iron and aluminum hy-

droxides are filtered off, and the precipitate is washed with warm water. The filtrate is acidified with 0.5 *N* hydrochloric acid, the solution neutralized to sofno red or *p*-nitrophenol indicator by addition of sodium hydroxide drop by drop, and the boric acid determined by titration with sodium hydroxide in the presence of mannitol or glycerol with phenolphthalein indicator. Time is saved by carrying out this titration separately from the main solution.

TITRATION OF BORIC ACID. The solution from the precipitation of iron and aluminum is acidified with hydrochloric acid and then just neutralized cautiously with standard sodium hydroxide to the yellow color of sofno red or *p*-nitrophenol. About 10 drops of phenolphthalein indicator and 25 to 50 cc. of neutral glycerol or mannitol (according to the amount of boric acid titrated) are added, and then the standard alkali added until a distinct reddish pink color appears. The true end point for boric acid is pH 11.

NOTE. The boric acid in the solution recovered from the iron and aluminum precipitate is determined also as directed above, and the amount added for total percentage of boric oxide.

1 cc. of *N* = 0.03482 g. B₂O₃; or 0.9536 g. Na₂B₄O₇ · 10H₂O; or 0.0618 g. H₃BO₃
 1 cc. of 0.5 *N* NaOH = half above amounts

The acid extraction generally effects complete solution of the borates available in crude borate minerals. Should silicoborates be present, a fusion of the acid residue should be made with sodium carbonate flux, and the fusion examined for borates.

The reflux condenser is used to avoid loss of the boric acid by volatilization. (The 6 *N* hydrochloric acid is approximately acid of constant boiling point.) This is unnecessary in water extractions for water-soluble borate.

The removal of iron and aluminum from the extract is necessary, as iron and aluminum salts lead to high results for boric acid by the action of their combined acid with the standard base.

Definite amounts of borate are invariably carried out by the iron and aluminum hydroxides, so that a recovery must be effected if the precipitates are present in appreciable amounts.

The isoelectric point of aluminum is between pH 6 and 7.5, and it is at this point that the aluminum compound is least soluble. Some aluminum hydroxide will go into solution if too much sodium hydroxide is added to precipitate the aluminum.

Therefore, care must be exercised in exactly neutralizing in the presence of a suitable indicator.

The end point in the presence of phenolphthalein is a combination of the two colors yellow and pink, and is a distinct reddish pink color. The sofno red or *p*-nitrophenol gives a distinct yellow color in alkaline solutions. Both indicators are colorless in acid solutions.

A concentrated solution of sodium hydroxide is used to neutralize the 6 *N* hydrochloric acid so as not to increase the volume for filtering. Other strengths or concentrations may be used.

Neutral glycerol is prepared as follows: To 1000 cc. of glycerol add 4 to 5 cc. of phenolphthalein and neutralize with regular sodium hydroxide reagent. Owing to the formation of acid, the color will fade, but addition of sodium hydroxide from time to time will keep the color pink. A sharper end point is obtained with mannitol.

If end points are run over, back titrations are possible with either indicator.

If a carbonate is used in the precipitation of iron and aluminum, it should be removed by acidifying the solution and gently heating at a "simmering" temperature for 10 to 15 minutes in a covered beaker. Loss of boron occurs if the beaker is not covered. The presence of carbonic acid in the solution leads to an error in the boric acid titration.

The use of sodium hydroxide in place of sodium carbonate in the precipitation of iron and aluminum avoids the necessity of removing carbon dioxide from the solution.

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RECEIVED September 29, 1931.

² The addition of 2 to 5 grams of sodium chloride hastens settling of the suspended material. The salt does not interfere with the accuracy of the method.

³ One gram of the residue occupies a volume slightly less than 0.5 cc. Generally the amount is so small that this additional water is unnecessary.

Determination of Carbon Dioxide and Titratable Base in Sea Water

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THAT carbon dioxide and carbonate salts play an important role in numerous chemical reactions and equilibria of sea water has long been recognized by oceanographers. As a consequence the quantities and chemical relations of these substances in sea water have been investigated during many years by a number of workers and many methods for the determination of carbon dioxide and titratable base have been proposed. In spite of this, the existing methods for the direct determination of carbon dioxide in sea water are too cumbersome and time-consuming, especially when it is realized that most oceanographic investigations require numerous analyses, often under difficult working conditions. Many titration methods have been used for determining the titratable base content and, in some cases, carbonate and bicarbonate, but these methods have not been sufficiently standardized and there is no unanimity of opinion as to the exactness and significance of the results obtained.

At the Scripps Institution information concerning the free and combined forms of carbon dioxide in the adjacent sea was desired in connection with studies of the biological environment and in the course of investigations of the calcium carbonate equilibrium of sea water. The authors have found that of the factors governing this equilibrium, the titratable base and the total carbon dioxide, together with the hydrogen-ion concentration, seem to be most readily susceptible of exact measurement. In a subsequent article (7) it will be shown that a distinct advance in the solution of the carbonate equilibrium problem has been made by expressing the buffer mechanism of sea water in terms of pH, carbon dioxide, and titratable base.

Accordingly, during the past several years, work has been carried out in this laboratory to develop a relatively simple and rapid method for the determination of total carbon dioxide in sea water, and we believe that this has been accomplished by adapting the Van Slyke (23) manometric method to the purpose. At the same time a critical study has been made of a method for measuring the titratable base content and of a differential titration method for determining the different forms of carbon dioxide.

DETERMINATION OF TOTAL CARBON DIOXIDE

Up to the present the total carbon dioxide in sea water has been determined, in practically all cases, either by titration

A semi-micromethod for determining the total carbon dioxide content of sea water with the portable manometric apparatus of Van Slyke is described. It is relatively simple, rapid, and suitable for work on board ship, and gives results reproducible to 1 per cent or better. A table of factors for converting the analytical data into milliliters, milligrams, or millimoles per liter of sea water is given.

The results of critical studies of the differential titration method for determining carbonate, bicarbonate, and free carbon dioxide in sea water are reported. When phenolphthalein and methyl orange are used as indicators and when the titrations are carried to end points in accord with theory, this method gives results reproducible to within 1 per cent, and the total carbon dioxide found agrees to about 1 per cent with that obtained with the Van Slyke apparatus.

It is shown that for sea water more alkaline than pH 7.8, the difference between the base titration value and the total carbon dioxide gives the carbonate content.

or by acidifying the water and expelling the gases by boiling or aërating, the quantity of carbon dioxide in the expelled gases being ascertained by one of several methods. The boiling-out method was used by Tornøe (20), who acidified the water with sulfuric acid and caught the carbon dioxide in a solution of barium hydroxide of known strength. Wells (25) determined carbon dioxide in water from the Gulf of Mexico by boiling 250 ml. of acidified water for some time and washing out the residual gas with a stream of carbon dioxide-free air, the carbon dioxide evolved being trapped in soda-lime weighing tubes. Thompson and his co-workers (19) used 4-liter samples of water which were acidified with hydrochloric acid and the carbon dioxide expelled into standard barium hydroxide solution by aërating for 24 hours. In more recent determinations in Thompson's laboratory (18), the gas was driven off by boiling, but the volume of the sample used is not stated. The principle of the Toricellian vacuum was introduced by Pettersson (15) who also added the feature of washing out the residual carbon dioxide with a stream of hydrogen generated within the water sample itself. Subsequently many investigators, among whom may be mentioned Dittmar (3) and Fox (5), have modified and improved Pettersson's method. The best method of this type is probably that developed by Fox.

The above methods all suffer from one or more defects which render them impracticable for use in most oceanographic investigations. The apparatus required is complicated and consequently the technic difficult or, on board ship, perhaps impossible; the time needed for a determination is too great to permit numerous analyses, the minimum time required, that of Fox's method, being a half hour or more; and finally, large water samples, ranging from 100 to 4000 ml. are necessary.

In many instances the necessity of using large samples of water is perhaps of no moment, but where analyses are to be made on water from below the sea surface or where many substances are to be determined on each sample, it becomes decidedly important to keep the volume of water required for each analysis down to a small figure. It is obvious that before we can expect adequate information concerning the variation with depth, season, and other factors of the quantity of carbon dioxide in various parts of the sea, a relatively simple and rapid method of analysis of the micro type must be developed. This is in keeping with the trend of development

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of other chemical methods employed in oceanographic studies.

A start in this direction was made by McClendon (13) who adapted the Van Slyke volumetric blood gas apparatus to sea water, making use of a 10-ml. sample. With this apparatus the dissolved gases are liberated by forming a vacuum, and their volume is subsequently measured at atmospheric

pressure. This method falls far short of the criterion of simplicity, however, as is shown by the following quotation from McClendon (13, p. 259).

With careful manipulation, an accuracy of 0.5 per cent was attained. In order to accomplish this, a large number of corrections had to be applied, and since these corrections vary so much for different determinations, they cannot be combined in a table such as Van Slyke has made for blood,....

The new manometric blood gas apparatus of Van Slyke and Neill (23), in which the gas is liberated

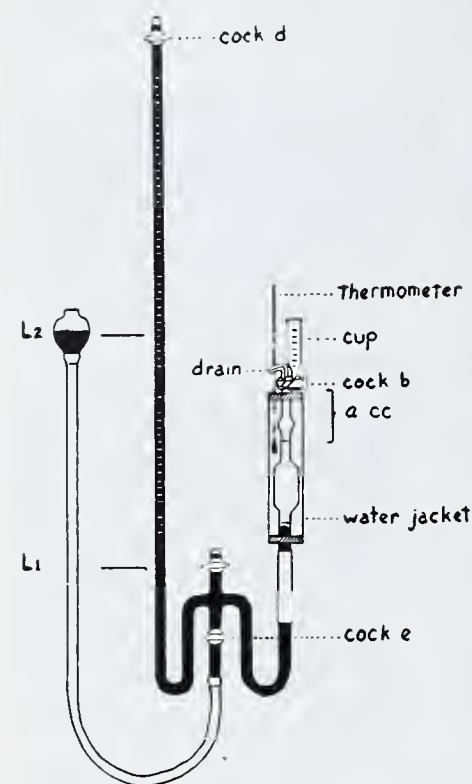


FIGURE 1. DIAGRAM OF GLASS PARTS OF APPARATUS

in a Toricellian vacuum, then reduced to a constant volume and its pressure determined, instead of measuring its volume at atmospheric pressure as in the old type of apparatus, offered the possibility of being adapted to the determination of carbon dioxide in sea water with sufficient speed and accuracy to meet the requirements of oceanographic work. Experiments with this apparatus were begun in this laboratory several years ago, and since then several hundred carbon dioxide determinations on sea water have been made. The apparatus, technic, and correction factors used are described below.

The apparatus used is the portable model (22), with a 50-ml. reaction chamber. A working diagram of the glass parts is shown in Figure 1. Before adding the sample, the cup is filled to the 6-ml. mark with an approximately normal solution of lactic acid. After lowering the mercury bulb to the position L_1 , cock e is opened and then the lactic acid slowly admitted into the reaction chamber by opening cock b . Cock b is again closed and sealed with a few drops of mercury before air is drawn into the apparatus, then the mercury is lowered until it fills only about half the reaction chamber, when cock e is closed. The chamber is then shaken slowly for about a minute and the lactic acid expelled by placing the mercury bulb at the level L_2 , and opening cock e and then cock b to the drain. Care is taken to close b before the mercury overflows. The washing is then repeated with an equal volume of distilled water. At the end of this washing a little mercury is allowed to run into the drain tube to make a mercury seal.

The apparatus is now ready for introducing the sample. About 1 ml. of mercury is caused to run into the cup by opening cock e , placing the mercury bulb at L_2 , and opening b carefully. Any water entering the cup with the mercury is removed with a piece of filter paper. For measuring and introducing the water sample, a 10-ml. pipet, accurately calibrated to deliver between marks and with a stopcock sealed to either the upper or lower end, is used (see Figure 2). This pipet is rinsed twice with the water to be analyzed and filled to above the 10-ml. mark. A rubber tip like that shown in Figure 2 is placed on the end of the pipet, and the level of the sample adjusted to the upper calibration

mark. The stopcock is then closed and, if a drop of water hangs from the tip, it is wiped off. The tip of the pipet is now introduced into the cup beneath the mercury, and fitted firmly against the bottom to make an air-tight seal. If an air bubble is trapped during the insertion of the pipet, it can be observed in the capillary portion of the cup and should be removed by gently manipulating the leveling bulb with cocks e and b open.

The mercury bulb is now placed at L_1 , cock e is opened, and then the stopcock of the pipet. Lastly cock b is carefully opened and the sample allowed to run slowly into the reaction chamber until the lower calibration mark of the pipet is reached, when cock b is closed. The pipet is then closed and quickly removed without allowing the tip to touch the sides of the cup. One milliliter of carbon dioxide-free 0.2 N lactic acid² is now run into the cup on top of the mercury. If air bubbles are noticed in the capillary part of the cup, they are removed by means of a wire, and then the mercury and acid are carefully lowered into the reaction chamber by opening cock b . The leveling bulb is at L_1 and cock e is open.

With a pipet a few drops of mercury are introduced into the cup to make a leak-proof seal. The leveling bulb is lowered until the mercury in the reaction chamber reaches the 50-ml. mark. Cock e is then closed, the leveling bulb placed at L_1 , and the mechanism which shakes the reaction chamber is started. Shaking is discontinued after 3 minutes when, with the mercury bulb still at L_1 , cock e is opened and the mercury allowed to rise, rapidly at first and then more slowly, until the liquid is exactly on the 2-ml. mark. Cock e is then closed and the manometer reading is taken. This reading is recorded as p_1 . Oscillation of the gas is to be avoided (23).

After reading the manometer, 0.2 ml. of 5 N sodium hydroxide is introduced into the cup over the mercury seal, and after making sure that no gas bubbles are in the capillary, is run into the reaction chamber by opening cock b , cock e remaining closed. After introducing the alkali, a new mercury seal is made, cock e is opened, and the mercury in the chamber lowered to about the 25-ml. level. Cock e is then closed and the reaction chamber agitated gently for about 1 minute, after which e is again opened and the liquid allowed to ascend to the 2-ml. mark, when the manometer is read, the reading being recorded as p_2 .³ The thermometer in the water jacket surrounding the reaction chamber is now read. The two manometer readings and the thermometer reading comprise the experimental data required for calculating the carbon dioxide content of the sea water analyzed.

From the manometer readings and the corresponding temperature, the quantity of carbon dioxide in the sample analyzed can be computed by means of the following equation, taken from Van Slyke and Neill (23):

$$V_0^{\circ, 760} = P \times \frac{a i}{760(1 + 0.00384t)} \times \left(1 + \frac{S}{A - S} \alpha'\right)$$

where $V_0^{\circ, 760}$ = volume of carbon dioxide measured under standard conditions; P = partial pressure of carbon dioxide—i. e., $p_1 - p_2$; a = volume of gas at which the pressure is measured; i = reabsorption coefficient of the gas in the liquid in the reaction chamber; t = temperature at which the manometer readings are made; S = volume of sample and reagents; A = volume of extraction chamber; and α' = the distribution coefficient of carbon dioxide between the gas and liquid phases.

Table I. FACTORS FOR CALCULATING CO_2 CONTENT OF SEA WATER

(When $A = 50$ ml., $S = 11$ ml., $a = 2$ ml., and sample = 10 ml.)

TEMP. ° C.	α'	FACTORS FOR CO_2 PER LITER OF SEA WATER		
		Ml.	Mg.	Millimoles
15	0.946	0.3209	0.6341	0.01442
16	0.922	0.3176	0.6279	0.01427
17	0.901	0.3151	0.6228	0.01416
18	0.8815	0.3125	0.6178	0.01404
19	0.864	0.3103	0.6134	0.01394
20	0.848	0.3079	0.6086	0.01383
21	0.829	0.3057	0.6042	0.01373
22	0.812	0.3033	0.5995	0.01362
23	0.794	0.3011	0.5950	0.01352
24	0.772	0.2984	0.5899	0.01341
25	0.756	0.2962	0.5854	0.01331
26	0.737	0.2940	0.5810	0.01321
27	0.720	0.2918	0.5765	0.01311
28	0.701	0.2896	0.5723	0.01301
29	0.683	0.2873	0.5676	0.01290
30	0.665	0.2854	0.5641	0.01282

² The carbon dioxide is removed in the Van Slyke apparatus after which the solution is kept under oil. (See Van Slyke and Neill, 23.)

³ To this reading Van Slyke and Neill (23) apply a correction, c , for the effect of the absorbent solution, but when only 0.2 ml. of sodium hydroxide solution is used the effect becomes negligible and no correction is necessary.

When the determination is made according to the procedure described above—i. e., when $A = 50$ ml., $S = 11$ ml., $a = 2$ ml., and the sample analyzed = 10 ml.—the factors given in Table I can be used for making the calculations. Volumes other than those given may be used provided the ratios $A:S:a$: sample remain unchanged. Multiplying $p_1 - p_2$ by the appropriate factor for the temperature at which the manometer readings were made will give the quantity of carbon dioxide per liter, in terms of milliliters, milligrams, or millimoles, respectively, in the sea water analyzed.

In computing the factors in this table, the value of i was taken as 1.017 (24) and applies only when the gas pressure is measured at one-twenty-fifth the volume of the reaction chamber—i. e., at 2 ml. in a 50-ml. chamber. The values for α' were computed from data given by Bohr (1) for the solubility of carbon dioxide in sodium chloride solutions, and are considered sufficiently accurate for sea water. In order to facilitate the computation of factors for apparatus for which the factors in the table cannot be used, Table I also gives values of α' for temperatures between 15° and 30° C.

Determinations of carbon dioxide in sea water by the procedure outlined above are readily reproducible to within 1 per cent, and the results obtained agree well with those obtained by other methods (see Tables II and III). Approximately 15 minutes are required to complete an analysis. The apparatus can readily be mounted on board ship, thus providing a means for making accurate and rapid determinations of carbon dioxide on extended cruises.

TABLE II. COMPARISON OF VAN SLYKE AND TITRATION METHODS ON SAMPLE TAKEN FROM SCRIPPS INSTITUTION PIER

TITRATABLE BASE	CARBON DIOXIDE BY TITRATION			Δ CO ₂ VAN SLYKE- TITRATION		
	Carbonate	Bicarbonate	Total	CO ₂ BY VAN SLYKE		
Milliequivalents	Mg./liter	Mg./liter	Mg./liter	Mg./liter		
2.291	11.89	77.03	88.92	89.59	0.67	
2.279	11.37	77.55	88.92	89.66	0.74	
2.279	11.37	77.55	88.92	88.95	0.03	
2.291	11.89	77.03	88.92	89.78	0.86	
2.291	12.20	76.41	88.61	89.78	1.17	
2.279	11.89	76.52	88.41	89.49	1.08	
2.303	12.20	76.93	89.13	89.31	0.18	
2.303	11.68	77.96	89.64	90.02	0.38	
2.284	11.89	76.72	88.61			
2.279	11.89	76.52	88.41			
2.303	12.20	76.93	89.13			
Mean	2.289	11.86	77.01	88.87	89.57	0.64

TABLE III. COMPARISON OF VAN SLYKE AND TITRATION METHODS ON SAMPLES FROM DEPTHS INDICATED 10 MILES OFF SCRIPPS INSTITUTION PIER ON AUGUST 20, 1931

DEPTHS Meters	TITRATABLE BASE Milli- equivalents	CARBON DIOXIDE BY TITRATION			Δ CO ₂ VAN SLYKE- TITRATION	
		Carbonate	Bicarbon- ate	Total	CO ₂ BY VAN SLYKE	
		Mg./liter	Mg./liter	Mg./liter	Mg./liter	
0	2.244	8.07	82.70	90.77	90.19	-0.58
5	2.232	7.76	82.80	90.56	90.77	+0.21
10	2.232	7.76	82.80	90.56	90.77	+0.21
15	2.237	7.76	83.01	90.77	91.45	+0.68
20	2.232	8.28	81.76	90.04	90.44	+0.40
25	2.232	7.76	82.80	90.56	90.76	+0.20
30	2.232	8.07	82.18	90.25	90.83	+0.58
35	2.232	7.76	82.80	90.56	90.68	+0.12
40	2.244	6.21	86.42	92.63	91.40	-1.23
50	2.244	5.69	87.46	93.15	94.46	+1.31
60	2.244	4.14	90.56	94.70	95.64	+0.94
75	2.249	2.58	93.87	96.45	96.61	+0.16
100	2.256	2.07	95.22	97.29	97.86	+0.57
150	2.256	1.04	97.29	98.33	99.71	+1.38
200	2.279	0.00	100.39	100.39	101.20	+0.81
Free CO ₂						
250	2.291	0.80	100.91	101.71	102.35	+0.64
300	2.291	2.00	100.91	102.91	101.98	-0.93
400	2.298	2.00	101.22	103.22	104.05	+0.83
500	2.303	3.60	101.43	105.03	105.06	+0.03

MEASUREMENT AND SIGNIFICANCE OF TITRATABLE
BASE OF SEA WATER

One of the most readily determined chemical properties of sea water is the amount of base which can be titrated with a strong acid to the turning point of some appropriate in-

dicator. Such titrations have long been in use, but there still remain many disputed points as regards both the methods and the significance of the results.

Even the names that have been given to the titratable base of sea water are at present not wholly satisfactory. By Tornøe (20), Fox (5), Ruppin (16), Buch (2), Kändler (10), and others it is designated as the "alkalinity," a term which would ordinarily suffice were it not that it is sometimes applied to the hydroxyl-ion concentration of sea water. McClendon (14) uses the expression "alkaline reserve," but this has a specific meaning in blood chemistry which is not equivalent to the titratable base of sea water. In a recent article, Thompson and Bonnar (18) propose the term "buffer capacity," but we feel that this may be confused with Van Slyke's (21) "buffer value" or "buffer index," which is defined as the rate of change of pH with the addition of alkali or acid and is obviously not comparable to the titratable base. Since none of the above terms appears to be entirely satisfactory, we are using the expression "titratable base" to designate the base combined with weak acid radicals in sea water, or, stated in another way, the quantity of base which can be titrated with a strong acid when the titration is carried to a point at which all the weak acid radicals have been replaced by the acid added.

We may now turn to a consideration of the methods in use for determining the titratable base. These may be grouped into back titration and direct titration methods. In the back titration methods a measured quantity of strong acid, in excess of the amount required to break up the salts of the weak acids, is added to a sample of sea water, the carbon dioxide liberated from the carbonates is boiled off, and the excess acid is titrated. For this titration, Tornøe (20) employed sodium hydroxide, and Fox (6) barium hydroxide, both using phenolphthalein as indicator. Ruppin (16) determined the excess acid by titrating the iodine liberated on the addition of a mixture of potassium iodide and potassium iodate. Thompson and Bonnar (18) have recently described a method whose principle is "to add a measured quantity of standard acid to a known amount of freshly sampled sea water, determine the hydrogen-ion concentration of the resultant solution, using special standards for comparison, and calculate the amount of acid neutralized." The pH is determined colorimetrically, the standards being prepared by adding known quantities of standard acid to neutralized sea water of the same chlorinity as the water analyzed.

In the case of the direct titration methods, standard acid is added to the turning point of an appropriate indicator, usually methyl orange. McClen-



FIGURE 2. PIPET
FOR MEASURING
AND INTRODUC-
ING WATER SAM-
PLE

don (14) modified this procedure by boiling off the carbon dioxide during the titration and using bromocresol purple as indicator. McClendon states that his method gives slightly higher results than does the usual back titration to the turning point of phenolphthalein.

DETERMINATION OF CARBON DIOXIDE BY TITRATION

The classical procedure, based on the work of Lunge (12) and of Küster (11), for determining the carbonate and bicarbonate content of natural water, is to titrate with standard hydrochloric or sulfuric acid to the turning point of phenolphthalein, then to add methyl orange (or a similar indicator), and continue the titration to the turning point of the latter indicator. According to the theory of this method, the carbonate content of the water can be computed from the phenolphthalein titration and the bicarbonate content from the second titration, whereas the total titration gives a measure of the titratable base. This method has been used by Dole (4) and for some years at the Scripps Institution for determining carbon dioxide in sea water. In this laboratory the procedure is as follows:

With a pipet a 100-ml. sample of sea water is measured into a 250-ml. Florence flask which has been rinsed with carbon dioxide-free distilled water, care being taken to keep the contact of the sea water with air at a minimum. While the pipet is being emptied, 4 to 6 drops of phenolphthalein (1 per cent solution in alcohol) are introduced into the flask, so that the indicator will be mixed with the sample without additional stirring.

If the phenolphthalein shows more than a faint trace of color, the sample is titrated with standard hydrochloric acid, approximately 0.015 *N*, using for comparison a blank of 100 ml. of distilled water in a flask similar to the one containing the sample. At first the acid is added rapidly and is mixed with the sample by gently rotating, rather than by shaking the flask, in order to have as little contact as possible between the air and the sample. The end point is taken as the last faint color before the solution is definitely colorless. A number of times we have determined the pH of this end point and found it to be 7.70 \pm 0.05, when corrected for salt effect.

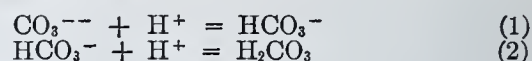
When the sample is acid to phenolphthalein, it is titrated with standard sodium carbonate of about the same normality as the hydrochloric acid. This titration is carried to the same end point and the same precautions against contact with air are taken as described for the hydrochloric acid titration.

After the buret reading for the phenolphthalein titration has been taken, 4 drops of methyl orange solution (0.05 per cent in distilled water) are added to the sample in the flask and the titration continued until the color of the methyl orange matches that of a blank. This blank is prepared by adding 4 drops of methyl orange to 100 ml. of a sodium chloride solution of approximately the same concentration as the sea water to be titrated, and then introducing about the same quantity of carbon dioxide that is liberated in the sample during the titration. It appears that bubbling air from the lungs through the solution will produce the proper concentration of carbon dioxide. The use of this comparison solution was introduced by Küster (11), and we have found its pH to be close to 4.5.

Sea water, such as may be used for experimental purposes, that has a higher or lower carbon dioxide content than ordinarily found in nature, should be sampled under oil to prevent loss or gain of carbon dioxide through contact with air. When making the phenolphthalein titrations of such water, a portion of the standard acid or alkali should be added to the flask before the sample is measured into it. It need not be stated, perhaps, that determination of carbon dioxide or titratable base should be made on freshly sampled water, because when water is stored, even in tightly stoppered bottles with practically no air space, biological activity will soon alter the carbon dioxide content, and basic substances may dissolve from the glass.

Since these titrations involve no abrupt changes in pH, the indicator colors must be judged very accurately if reproducible results are to be expected. It is essential, also, that the end points be in close agreement with those deduced from the theory of titration for the respective substances determined. It has already been stated that the end points to which we titrate occur at about pH 7.7 for the phenolphthalein titration and at pH 4.5 for the methyl orange titration. It can readily be shown

that these values agree well with theory. The reactions involved in the titration with hydrochloric acid are:



For Reaction 1 the titration, to give correct results, should be carried to the pH of a solution of bicarbonate in sea water. The mass law equation obtained by combining the two dissociation steps, is:

$$K_1' \cdot K_2' = \frac{[\text{H}^+]^2 [\text{CO}_3^{--}]}{[\text{H}_2\text{CO}_3]}$$

In a solution containing only bicarbonate, $\text{CO}_3^{--} = \text{H}_2\text{CO}_3$, and

$$[\text{H}^+] = \sqrt{K_1' \cdot K_2'}, \text{ or } \text{pH} = \frac{1}{2} (pK_1' + pK_2')$$

In a following paper (7) it is shown that for sea water the dissociation constants of carbonic acid, in the usual logarithmic terms, are close to the values of $pK_1' = 6.0$ and $pK_2' = 9.0$. According to the above equation, these constants would lead to a pH of 7.5 for the theoretical end point of Reaction 1, whereas we titrated to a pH close to 7.7.

The theoretical end point for the methyl orange titration, according to Reaction 2, is given by the relation,

$$[\text{H}^+] = \sqrt{K_1' \cdot [\text{H}_2\text{CO}_3]} \text{ or } \text{pH} = \frac{1}{2} (pK_1' - \log [\text{H}_2\text{CO}_3])$$

If the value of the carbonic acid is taken as the amount of carbon dioxide ordinarily present in sea water—namely, about 2.2 millimoles per liter, then:

$$\text{pH} = \frac{1}{2} (6.0 + 2.7) = 4.35, \text{ as against } 4.5 \text{ found}$$

There is thus an excellent agreement between the end points deduced from theory and those developed experimentally. These end points also have the advantage of being easily identified during titration.

A number of objections have been leveled against titration methods for determining carbonates and carbon dioxide, especially of sea water. The most serious objection is usually against the phenolphthalein part of the titration, but Thompson and Bonnar (18) also question the titration to methyl orange as a means of determining the titratable base. Their objection is based on a comparison of results obtained by their own method with results obtained by titrating to methyl red, methyl orange, and bromophenol blue. As shown in Table IV of their paper, the agreement between their method and the methyl orange titration is better than in the case of the other methods tested, and the departure is significant only in the first and last samples of the six listed. Johnston (9) states that the methyl orange titration of the titratable base is reproducible and accurate when the Küster comparison method for determining the end point is employed. Admittedly the color changes of the whole titration procedure outlined are difficult to judge, and considerable training is required to obtain concordant results. However, the Küster comparison method almost automatically leads to a proper end point, and we have already pointed out the excellent agreement between the theoretical and measured pH of the end point.

The objections to phenolphthalein as an indicator for the titration of carbonate have been summed up by Johnston (9, p. 961), who says:

Direct titration with acid and phenolphthalein is not to be recommended. For.... the results depend greatly on what one chooses as the point at which the solution is considered to have become colorless....

This effect, Johnston points out, depends upon the slow rate of neutralization of carbonic acid, which occasions the repeated vanishing and reappearing of the color. Another factor of importance in all titrations of the salts of carbonic acid is the loss of carbon dioxide when this gas is in excess of the partial pressure of the gas phase. Thus Johnston notes that

Seyler (17) found that errors in the phenolphthalein titration are due chiefly to loss of carbon dioxide, so that by carrying out the titration in a closed flask, sharper end points and better results were obtained. For determining carbonate and bicarbonate in a mixture of these salts, Johnston recommends first titrating to the methyl orange end point and then determining the bicarbonate by precipitation with an excess of alkali and barium chloride, the excess of alkali being measured by back titration. This method is obviously not applicable to sea water because of the magnesium and calcium present.

Although our experience indicates (see Tables II and III) that titration to phenolphthalein, provided the proper precautions are taken, will give results of a satisfactory order of accuracy for sea water, a substitute method may at times be useful, especially for checking the titration method. Such a method is provided by the fact that from the total carbon dioxide, as determined by the Van Slyke apparatus, and the titratable base, the respective amounts of carbonate and bicarbonate can be computed. In sea water which contains only negligible amounts of carbonic acid and certain other substances to be mentioned later, the following are the equations for titratable base and total carbon dioxide:

$$\begin{aligned} B &= \text{HCO}_3^- + 2\text{CO}_3^{--} \\ T \text{ CO}_2 &= \text{HCO}_3^- + \text{CO}_3^{--} \end{aligned} \quad (3)$$

where B is the titratable base in milliequivalents or other appropriate units, and $T \text{ CO}_2$ is the total carbon dioxide expressed in comparable terms. Then, subtracting 4 from 3, we obtain,

$$B - T \text{ CO}_2 = \text{CO}_3^{--} \quad (5)$$

The bicarbonate is obviously given by the relation

$$T \text{ CO}_2 - \text{CO}_3^{--} = \text{HCO}_3^- \quad (6)$$

We thus have a means of determining the carbonate and bicarbonate carbon dioxide fractions of certain sea waters even when titration with phenolphthalein is not practicable, and we also have a method for testing the validity and accuracy of the differential titration method. The results of such a test series are given in Table IV, where carbonate and bicarbonate values determined by titration are compared with values obtained according to Equations 5 and 6. It will be noted that the agreement between the two methods is consistently good.

TABLE IV. COMPARISON OF CARBONATE VALUES DETERMINED BY TITRATION AND COMPUTED FROM TITRATABLE BASE AND TOTAL CO_2

(Data given in Table II used)

TITRATABLE BASE EXPRESSED AS CO_2 (B)	TOTAL CO_2 BY VAN SLYKE ($T \text{ CO}_2$)	CARBONATE CO_2 BY $B - T \text{ CO}_2$	CARBONATE CO_2 BY TITRATION	DIFFERENCE
Mg./liter	Mg./liter	Mg./liter	Mg./liter	
100.81	89.59	11.22	11.89	0.67
100.30	89.66	10.64	11.37	0.73
100.30	88.95	11.35	11.37	0.02
100.81	89.78	11.03	11.89	0.86
100.81	89.78	11.03	12.20	1.17
100.30	89.49	10.82	11.89	1.07
101.33	89.31	12.02	12.20	0.18
101.33	90.02	11.31	11.68	0.37

The evaluation of carbonates and bicarbonates from the total carbon dioxide and the titratable base is possible only when negligible quantities of carbonic acid are present, and this would be the case in water containing CO_3^{--} , and when the titratable base occurs solely as salts of carbonic acid. That there are traces of other substances in sea water which are capable of forming weak acids has long been known. These are chiefly silica, boron, and phosphorus. The amount of phosphorus is known to be too small to be a factor, and in this and many other localities the same is true of silicon.

Concerning boron in sea water there is practically no information available, but it is thought that the quantity is negligible. Irving (8) goes to the length of maintaining that about half the buffer value of sea water is due to factors other than the salts of carbonic acid. Thompson and Bonnar (18) "are of the opinion that the buffer capacity is also a function of some inherent basic property of the sea."

However, experimental data seem to disprove both of these contentions, at least as far as certain parts of the ocean are concerned. If the contribution of the "nonvolatile" buffer—i. e., salts other than those of carbonic acid—to the titratable base of sea water were of numerical importance, the total carbon dioxide as determined by a direct method should be consistently lower than that determined by titration. That this is not the case can be seen from Tables II and III which show that the agreement between the two methods is as good as the agreement between different determinations by either method. In this connection, reference should be made also to the work of Dole (4) and of Wells (25) on water from the Gulf of Mexico. Dole determined carbon dioxide by titration and his results were corroborated by Wells who used a direct method already mentioned.

Moreover, when the pH of sea water is increased by removing carbon dioxide, the nonvolatile buffer effect should increase very appreciably and reach a value of about 20 per cent of the base titration at pH 9.5. In a following paper (7) the results of some experiments will be reported in which the pH of sea water was brought to this figure by the removal of carbon dioxide. Even on this water excellent agreement was obtained between carbon dioxide values determined directly and by titration.⁴ As a result we are led to the conclusion that the nonvolatile buffers are of no practical significance in natural sea water and that the titratable base is determined almost entirely by the quantity of salts of carbonic acid.

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⁴ Some weeks after this was written, carbon dioxide values obtained by titrating this water were too high and later analysis indicated that this was due to silica dissolved from the bottle containing the water.

Improved Direct Nesslerization Micro-Kjeldahl Method for Nitrogen

Determination in Organic Compounds and Biological Fluids

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LAURO (5) has recently described the use of selenium as a catalyst in macro-Kjeldahl digestions. He found that it is much superior to either copper or mercury. These results suggested to the writers the possibility of improving the micro-Kjeldahl method as it is applied in determining the nitrogen of biological fluids and of compounds.

The phosphoric-sulfuric acid digestion of Folin and Wu (2) has the disadvantage of severely attacking the digestion tubes and materials used to prevent bumping, leading to breakage and some difficulty in obtaining clear nesslerized solutions. The hydrogen peroxide-sulfuric acid digestion of Koch and McMeekin (4) is rather free from these objections, but there is the danger of spattering and loss of sample upon addition of peroxide to the hot digestion mixture, and there may be appreciable nitrogen in the peroxide which must be determined and corrected for. Also, the necessity of interrupting the digestion and adding the peroxide is an inconvenience.

It has been found that blood filtrates and urines are rapidly and completely digested by 1 to 1 sulfuric acid containing approximately 0.2 per cent selenium, and the nitrogen values are similar to those found by the peroxide method of Koch and McMeekin. The selenium does not interfere with nesslerization. By using a digestion mixture of 1 to 1 sulfuric acid saturated with potassium sulfate and 0.2 per cent selenium, the rate of digestion is increased, and such a mixture is preferable in the analysis of substances difficult to oxidize, although quite unnecessary for blood filtrates and urine.

EXPERIMENTAL PROCEDURE

REAGENTS. Selenium digestion mixtures:

1. Without potassium sulfate. One cubic centimeter of selenium oxychloride (Eimer & Amend) is added to 500 cc. of 1 to 1 sulfuric acid and mixed. This mixture is recommended for the determination of blood N. P. N., the nitrogen of urine, and other biological fluids. The solution should be kept stoppered when not in use to prevent taking up water and precipitation of selenium.

2. With potassium sulfate. One volume of sulfuric acid is mixed with an equal volume of saturated potassium sulfate solution, and to 500 cc. of this mixture 1 cc. of selenium oxychloride is added. A small amount of potassium sulfate separates overnight. The solution is decanted from this.

Nessler reagent: This was prepared according to Bock and Benedict (3) and then diluted with an equal volume of 10 per cent sodium hydroxide. This formula has been found quite satisfactory.

Hydrogen peroxide: Three per cent hydrogen peroxide from Parke Davis, and Merck's Superoxol. This was found to be practically nitrogen-free.

METHOD. A quantity of solution representing approximately 0.2 to 0.3 mg. of nitrogen (5 cc. of Folin-Wu blood filtrate or 1 cc. of urine diluted 1 to 40) is pipetted into a Pyrex digestion tube¹ (25 by 200 mm.) calibrated at the 50-

cc. level. To this 1 cc. of the digestion mixture and 2 dry glass beads (2 are better than 1) are added, and the tube covered with a glass bulb or light short-stemmed funnel with the stem sealed. The solution is rapidly evaporated over a microburner until all water is driven off, the mixture chars, and sulfate fumes appear. The flame is then reduced, the mixture gently boiled until it becomes clear and colorless (usually 1 to 2 minutes), and the boiling continued a further 4 minutes. The digest is cooled, diluted with 25 cc. of water, and 15 cc. of Nessler's reagent are added quickly.² The tube is diluted to the mark, stoppered with a rubber stopper, and mixed. A standard is prepared using 1 cc. of the digestion mixture and 0.2 to 0.3 mg. of nitrogen, nesslerized and diluted to 50 cc. Colorimetric readings and calculations are made in the usual way.

RESULTS

Table I records data obtained on tungstate filtrates of blood and diluted urines using 1 to 1 H₂SO₄ + 3 per cent H₂O₂, 1 to 1 H₂SO₄ + 30 per cent H₂O₂, and 1 to 1 H₂SO₄ + 0.2 per cent Se as the digestion mixtures. The values are identical within the limits of error of the methods. In running duplicates, the selenium method seems to give somewhat better checks than the peroxide method, possibly because of loss by spattering with the latter procedure.

TABLE I. DATA ON TUNGSTATE FILTRATES OF BLOOD AND DILUTED URINES

DIGESTION MIXTURE	(All determinations in duplicate)		
	1 to 1 H ₂ SO ₄ + 3% H ₂ O ₂ Mg. N/100 cc.	1 to 1 H ₂ SO ₄ + 30% H ₂ O ₂ Mg. N/100 cc.	1 to 1 H ₂ SO ₄ + 0.2% Se Mg. N/100 cc.
Blood filtrates:			
Sheep blood	50.5	50.5	50.5
Pig blood	37.7	37.0	37.0
Urines:			
Sample 1	1240	1220	1240
Sample 2	1120	1200	1140
Sample 3	1120	1120	1100
Sample 4	693	690	695

TABLE II. NITROGEN VALUES

DIGESTION MIXTURE	(All determinations in duplicate)				REMARKS
	NITROGEN FOUND IN:			N	
	K ₂ SO ₄ + H ₂ SO ₄ + 3% H ₂ O ₂ %	K ₂ SO ₄ + H ₂ SO ₄ + 30% H ₂ O ₂ %	K ₂ SO ₄ + H ₂ SO ₄ + 0.2% Se %	CALCD. %	
Urea	46.3	45.9	45.9	46.66	Unpurified
Uric acid	33.3	33.3	33.3	33.33	
Alanine	17.1	17.0	17.0	15.73	
Acetanilide	10.47	9.45	10.47	10.36	
Phenacetin	7.30	7.76	7.70	7.82	
Creatine	20.90	21.70	23.60	28.17	29.20% by macro-Kjeldahl using 0.2 gram of Se + 0.5 gram of sucrose
Creatine	23.20	25.00	29.40	28.17	2 mg. sucrose in each digestion
Creatinine	29.00	30.05	36.5	37.13	2 mg. sucrose in each digestion
Cystine	11.66	11.66	2 mg. sucrose in each digestion

Table II gives nitrogen values on several compounds. Inasmuch as only comparative results were desired, the compounds used, with one or two exceptions, were commercial samples and not specially purified. For these

² Nessler's reagent must be added quickly after water to prevent separation of elementary selenium with resulting cloudiness.

¹ Tubes constricted to about one-third diameter at the graduation mark were used. This enables more accurate dilution and also tends to minimize the loss of sulfate.

determinations the K_2SO_4 - H_2SO_4 -Se and K_2SO_4 - H_2SO_4 -peroxide digestion mixtures were used for comparison. Results with the 1 to 1 H_2SO_4 + Se mixture are quite comparable on these compounds to those obtained by using the K_2SO_4 - H_2SO_4 -Se mixture, as are also the 1 to 1 H_2SO_4 -peroxide mixtures, although the digestion may require a few minutes longer.

The nitrogen of creatine and creatinine is not given completely by any of the above digestions. However, recovery is attained by using the K_2SO_4 - H_2SO_4 -Se mixture + 2 mg. of sucrose. Here the presence of potassium sulfate, by raising the boiling temperature, markedly speeds up the rate of digestion; in fact, without it and using sucrose, not all of the nitrogen of creatine or creatinine was recovered. Neither 3 nor 30 per cent peroxide combined with sulfuric acid and potassium sulfate + sucrose gave all of the nitrogen of either creatine or creatinine. It seems, therefore, that the selenium method combined with sucrose is a little more effective on resistant compounds than the peroxide method. It should be noted that the addition of sugar with K_2SO_4 - H_2SO_4 -Se gives the same nitrogen values for urine as H_2SO_4 -Se. The creatinine is completely determined by the ordinary methods when admixed with the other substances of urine.

One-tenth per cent selenium gives rather satisfactory digestion but not quite as good as 0.2 per cent. Four-

tenths per cent is very little better than 0.2 per cent. The selenium digestion gives correct values in the presence of chlorides.

It was noted that there is much less tendency toward bumping in the selenium digestions than the others, probably because of the separation of elementary selenium (which redissolves as the acid becomes concentrated).

This work confirms that of Davenport (1) that 3 per cent peroxide may satisfactorily, and preferably from the standpoint of handling and cost, be substituted for the Superoxol recommended by Koch and McMeekin.

From the experience of the authors, the selenium method seems to be essentially free from the annoyances of the other methods and gives a little more consistent results than the peroxide method. The cost of the catalyst is insignificant, about 4.5 cents for 500 cc. of digestion mixture.

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The Photovoltaic Cell as Indicator in Precise Titrometry

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IN PREVIOUS communications (2-4), various methods employing the photoelectric cell for following titrations have been described or mentioned. Because of the feeble photoelectric currents obtained under most conditions, amplification has been necessary. In order to obtain increased sensitivity, gas-filled cells were usually employed and possibilities of instability and electrical leakage were sometimes troublesome to obviate. Obviously a method which would retain most of the advantages and a minimum of the disadvantages of former methods would be highly desirable. The dry types of so-called "photronic" cells which have been commercially obtainable for a few months, because of their favorable characteristics, have been chosen for use in the present method.

Although these cells are said to be "electronic" in action, their output is dependent upon the photovoltaic e. m. f. developed (1). For this reason, the author prefers to call them "photovoltaic" cells.

CELL CHARACTERISTICS

A few simple experiments conducted with one of these cells showed that in one respect, at least, it was far superior to the photoelectric cell—namely, stability. Also, the fact that its resistance under working conditions is comparable with that of medium-sensitivity portable galvanometers makes possible simple yet sensitive electrical arrangement. Simple experiments with filters showed that, spectrally, the

Because of its inherent stability and simplicity of operating requirements, the photovoltaic cell is admirably suited to precise titrometry, especially where the use of small samples is necessary. In the method herein described, precision of one part per thousand is obtained with three titrations. Under the most favorable conditions only five readings for each determination are necessary, and the end point is obtained by extrapolation.

cell was most sensitive in the yellow-green portion of the spectrum. It was also noted that some response was obtained in the near infra-red and ultra-violet. Later publication of technical data by the manufacturers giving relative spectral sensitivity bears out these conclusions, but unfortunately the makers do not state whether or not these values are based on

equal-energy considerations or are dependent on the intensity distribution of a particular type of source.

To gain further knowledge of the electrical characteristics of the cell under convenient working conditions, a 6-volt, 21-candle power, concentrated-filament, nitrogen-filled lamp was mounted on an optical bench, and the cell was mounted so that it might be moved with respect to the source. The data given in Table I were obtained as follows:

- D = distance between cell and source, cm.
- E = photovoltaic e. m. f., millivolts, measured by conventional Hildebrand potentiometric method.
- I = calculated current, microamperes, which would flow with cell short-circuited.
- R = corrected resistance of cell obtained by deducting resistance of measuring instruments from total circuit resistance.
- W = calculated power, millimicrowatts, dissipated by cell when short-circuited.

In order to understand better the relations between e. m. f., current, and power, respectively, with light intensity, their logarithmic values were plotted as shown in Figure 1. At the values of distance from the source corresponding to the lower

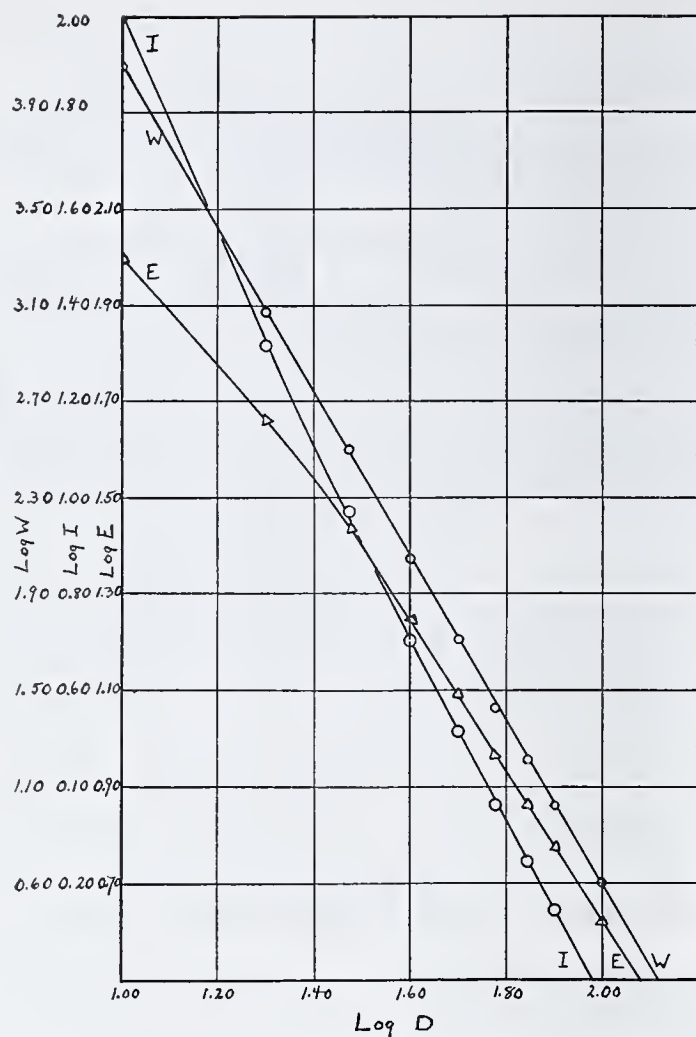


FIGURE 1. LOGARITHMIC VALUES OF E. M. F., CURRENT, AND POWER

light intensities, it will be noticed that all curves have a constant slope, and, since under these conditions we are justified in assuming the applicability of the inverse square law, the values in the second column of Table II may be considered approximately correct.

After considering the various usable characteristics, the next problem was to select the most convenient one for use in the proposed method. If a high level of illumination were possible, the current characteristic would be most suitable. Under actual conditions, however, instead of having available a strong intensity of white light, the filters used reduce the illumination to from 1 to 10 per cent of the original value in a narrow spectral band. Currents would thus be obtained which would require exceedingly delicate measuring instruments. The e. m. f. characteristic, besides being independent of cell resistance, makes possible the use of a null method which may employ a comparatively rugged portable galvanometer.

Instead of actually measuring the cell potential, it is evident that a definite fixed opposing potential may be pre-selected, and the light intensity falling on the cell may be varied until for each desired measurement the opposing potential is exactly equaled by the cell. Besides being convenient and economical, this method allows great flexibility. Its use is limited, of course, to the requirement of measuring a change rather than an absolute value. If reference standards are used, the method may be applied to absolute measurements when the proper precautions are taken.

APPARATUS AND ELECTRICAL CONSTANTS

To try out the method, the apparatus shown in Figure 2 was assembled as follows: *L* is a galvanometer illuminator containing a 64-candle power, concentrated-filament, nitro-

gen-filled lamp operating at 6 volts and supplied by a storage battery, *B*, of approximately 100 ampere hours capacity. The approximately parallel light from *L* passes through diaphragm *D* which is arranged so that its aperture may be read on scale *S* by means of vernier *V*. *S* is a 200-mm. galvanometer scale, and *V* is arranged to read it to a tenth of a millimeter. Cell *C*, containing the material to be titrated, and the indicator (if one is used) are next in the light path, followed by filter *F* and the light-sensitive cell *P*. Voltage divider *O* is arranged so that a small portion of the potential difference of *B* (about 100 millivolts, maximum) may be used to oppose the photovoltaic cell *P*. Galvanometer *G* indicates whether the balance has been obtained when tapping key *T* is closed. *G* has a sensitivity of about 150 mm. per microampere and is of the portable lamp and scale type.

To obtain an idea of the uniformity of response with scale reading, the values shown in Figure 3 were obtained. No filter or absorption cell (*C*) was used, and the potentials were obtained by the Hildebrand method. Values for lower scale readings are not given because their use in actual work is exceedingly limited, owing to the small photovoltaic response obtained.

ACIDIMETRY TITRATIONS

METHOD OF OPERATION. As a preliminary trial, the titration of sulfuric acid with 0.1 *N* sodium hydroxide was attempted. Phenolphthalein was chosen as the indicator, and a reasonably good square bottle of 150 ml. capacity was used as the titrating cell, *C*. Stirring was accomplished by carbon

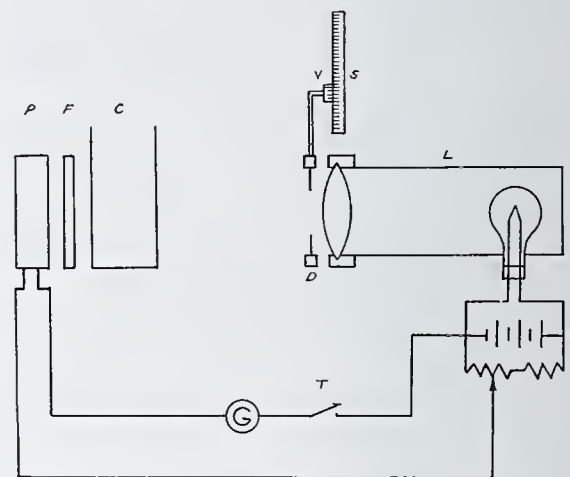


FIGURE 2. SCHEMATIC DIAGRAM OF APPARATUS AND ELECTRICAL CIRCUIT

dioxide-free air. The filter was chosen in the manner illustrated in Figure 4 of a previous communication (4). In this case, since phenolphthalein absorbs selectively in the green region, a green filter is necessary. Of the filters available, that designated by the Corning Glass Works as "Sextant Green" of 3.86 mm. thickness and transmitting between 840 μ and 580 μ , was selected as most suitable.

A sample of acid was pipetted into the titration cell *C* by means of a 5-ml. Bureau of Standards calibrated pipet. To this 100 ml. of carbon dioxide-free distilled water and 5 drops of 1 per cent phenolphthalein in alcohol (previously found to be the most desirable amount) were added. The first few titrations were made using a 50-ml. buret and some standard sodium hydroxide made up from commercially prepared standards. The apparatus seemed to function consistently, but fading of the end-point color and inability to get a definite equivalence value were traced to carbonate in the alkali. A new standard solution prepared in such a manner as to be practically carbon dioxide-free gave good results, but it was immediately noted that more accurate buret readings were necessary if the full benefits of the method were to be attained.

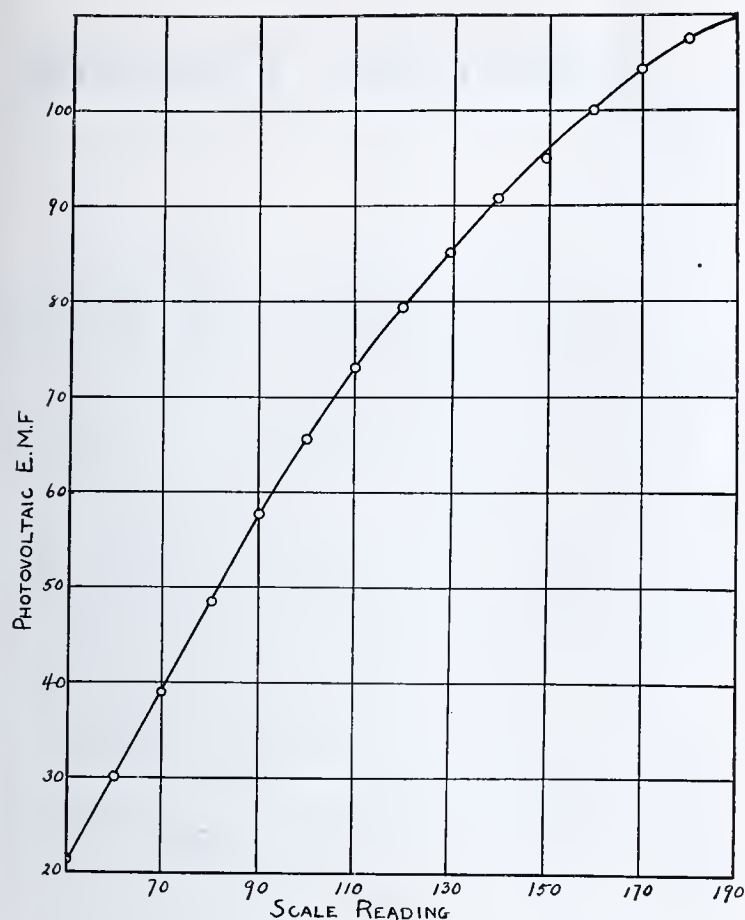


FIGURE 3. RELATION BETWEEN SCALE READING AND PHOTOVOLTAIC E. M. F.

A 5-ml. buret from which additions of 0.002 ml. could be estimated was substituted for the larger one, and five titrations, illustrated in Figure 4, were carried out. In each case, the opposing potential was set by *O* at such a value that the colorless solution caused the photovoltaic e. m. f. to equal the opposition when the scale reading was set between 80 and 90. Scale readings for additions of alkali were taken as shown in Figure 4. (Titration 5 was accidentally run by the end point so far that the color produced gave an off-scale value for the scale reading.) The results obtained on different days and by different observers are in very fair agreement and will not be discussed.

TABLE I. PHOTRONIC CELL CHARACTERISTICS

<i>D</i> Cm.	<i>E</i> Millivolts	<i>I</i> MAX. CALCD. Microamperes	<i>W</i> MAX. CALCD. Millimicro-watts	<i>R</i> CELL Ohms
10	98.7	100.4	9910	983
20	45.7	20.7	946	2221
30	27.3	9.38	256	2910
40	17.7	5.05	89.4	3400
50	12.4	3.28	40.6	3780
60	9.2	2.31	21.2	3980
70	7.3	1.77	12.9	4130
80	6.0	1.41	8.47	4250
100	4.2	0.97	4.08	4310

TABLE II. RELATIONS OBTAINED FROM FIGURE 1

$$E = K_1 \frac{1}{D^{1.55}} \quad E = K_4 C^{0.78}$$

$$I = K_2 \frac{1}{D^{1.85}} \quad I = K_5 C^{0.93}$$

$$W = K_3 \frac{1}{D^{3.39}} \quad W = K_6 C^{1.70}$$

C = light intensity

ERRORS AND PRECAUTIONS. The usual difficulties caused by buret and pipet drainage must be carefully considered. Temperature changes during the period of manipulation are to be avoided. Reagents and water must be carbon dioxide-free. The titration curves are probably not true straight lines, but may be considered so for these experiments. A typical curve is shown in Figure 3 of a communication by

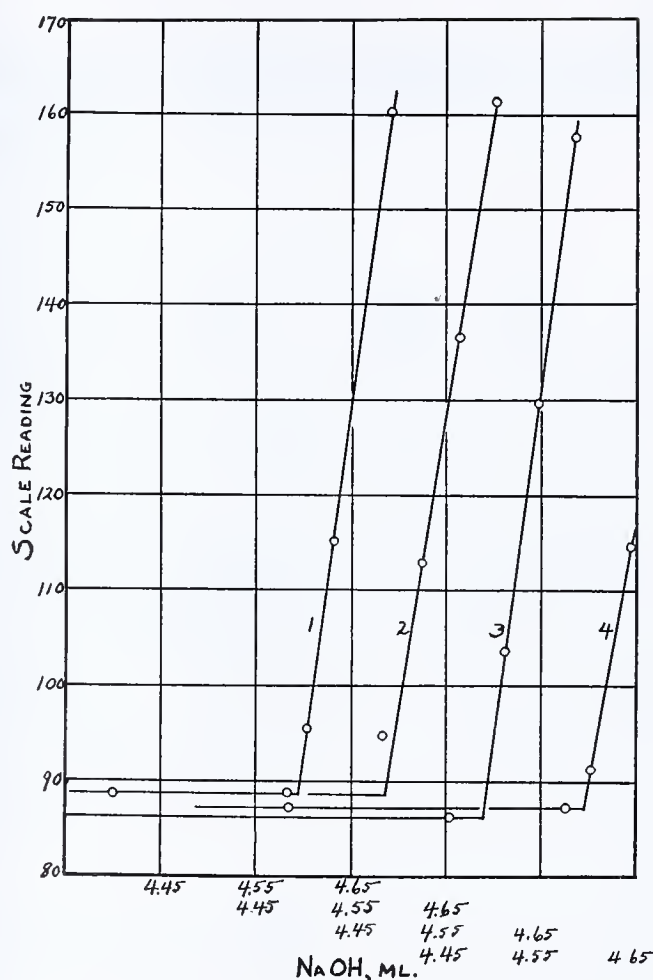


FIGURE 4. TITRATION MADE USING PHOTOVOLTAIC CELL

TITRATION	END POINT, NaOH ML.
1	4.595
2	4.585
3	4.587
4	4.595
Av. 4.590 \pm 0.0025	

Müller and Partridge (2), but owing to the enormous change at the end point, no curvature could be detected. It will also be noted that the slopes of the vertical portions are not the same. This is due to the fact that different starting points were selected and the illumination level was slightly different on different days. The light source should be constant during the period between successive readings. This was accomplished in a simple manner by allowing the storage battery *B* to be charged at a 5-ampere rate while being discharged by the lamp at the rate of 7.5 amperes. Under these conditions the source was remarkably constant over a period of several hours.

The efficiency of the optical system can be improved, and such improvement will make the device more sensitive in the red and violet regions than is the present model.

Many other determinations, both macro and micro in nature, have been undertaken and will be described in later communications.

ACKNOWLEDGMENT

The author wishes to express his indebtedness to R. A. Smith of this laboratory for his assistance in making many of the observations contained herein.

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RECEIVED March 3, 1932.

Apparatus for Pressure Control in Vacuum Distillations

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A COMMON difficulty in carrying out accurate distillations under vacuum is that of maintaining the pressure within sufficiently close limits. Of the many devices which have been suggested for overcoming this difficulty, probably the most satisfactory has been that of Cox (1), who used a manometer with an adjustable electrode so that, when the pressure had reached a desired value, contact was made between the electrode and the rising mercury surface, thus actuating a relay and shutting off the pump motor current. The apparatus to be described here is similar in principle to that of Cox, and requires, as did his, the use of a vacuum pump which will not leak or suck back oil when stopped while connected to an evacuated system. The manometer with the adjustable electrode is replaced, however, by another device which requires no machined parts or packing (although it is not stated, these appear necessary to insure satisfactory operation of the manometer which Cox has described), and provision is made for wiping out most of the pressure fluctuations.

The apparatus is illustrated by Figure 1. The "pressure balance" at the center, which replaces the previously mentioned manometer, is about 6 inches (15.24 cm.) tall and 7 inches (17.78 cm.) wide. The bulb on the left-hand vertical arm is about 1.5 inches (3.81 cm.) in diameter, the tube just below it 1 inch (2.54 cm.), and the rest of the tubing 7 mm. inside diameter. The relative positions of the sealed-in

the various parts of the apparatus. The relay used should be fairly rugged. For use with the prescribed voltages, one with about 100 ohms resistance will be satisfactory.

To operate the apparatus, stopcock *A* is closed, *B* and *C* are opened, and the pressure balance adjusted so that the right-hand sealed-in electrode just fails to make contact with the mercury. The pump motor is then started and the system evacuated to the desired pressure. Stopcocks *B* and *C* are then closed. Any further decrease in the pressure causes the mercury to rise in the right-hand vertical tube of the balance, completes the relay actuating circuit, and stops the pump motor. Stopcock *A* is then opened sufficiently to admit a stream of air which will keep the pump in operation about one-third of the time. Final adjustments of pressure are made by tilting the pressure balance—clockwise to increase pressure, counter-clockwise to decrease it. At the end of a distillation, stopcock *B* should be opened before admitting air into the system, as the entering air will otherwise bubble past the mercury into the bulb of the balance and may blow mercury into the upper horizontal tube.

The inertia of the moving pump and motor parts causes the pump to operate an additional stroke or so after the motor current is shut off, and these additional strokes of the pump are believed to be the main cause of the pressure fluctuations which occur in the apparatus. Presumably these could be overcome by using a sufficiently large volume in the system, but the arrangement illustrated gives exactly enough regulation with reservoirs of moderate volume. The introduction of the section of capillary tubing cuts down the rate of diffusion of the gas in the system so that a decrease in pressure in the left-hand bottle only slowly affects the pressure in the right-hand one, and when the apparatus is in operation such changes in pressure are compensated by the air admitted through stopcock *A* before any noticeable pressure change occurs in the right-hand bottle. The effect of the capillary is illustrated by the fact that only faint pressure changes can be detected when 250-cc. flasks are used instead of the size bottles specified.

The higher the pressure at which the system is operated, the greater the effect of the additional strokes of the pump, and hence the smaller the bore of the capillary used. For the usual range of distillation pressures, 10 to 150 mm., a 3-inch (7.62-cm.) section of 1.5-mm. bore capillary is satisfactory. For pressure in the neighborhood of 300 mm., a similar section of 0.3-mm. bore capillary has been used. At very low pressures, stopcock *C* can be left open.

Although leakage across stopcock *B* prevents satisfactory operation of the apparatus, the pressure difference between the two sides is so slight that this never occurs if a well-ground stopcock is used and kept well lubricated.

This type of control apparatus has been employed quite successfully in a number of installations in this laboratory. When the apparatus is properly adjusted, the pressure deviations are too small to be detected on an ordinary manometer, or to affect the rate or temperature of the distillation. Presumably the only changes needed to adapt the device to the control of pressures above atmospheric, up to the limit of the strength of the glass parts, would be the substitution of a suitable pressure pump for the vacuum pump and the reversal of

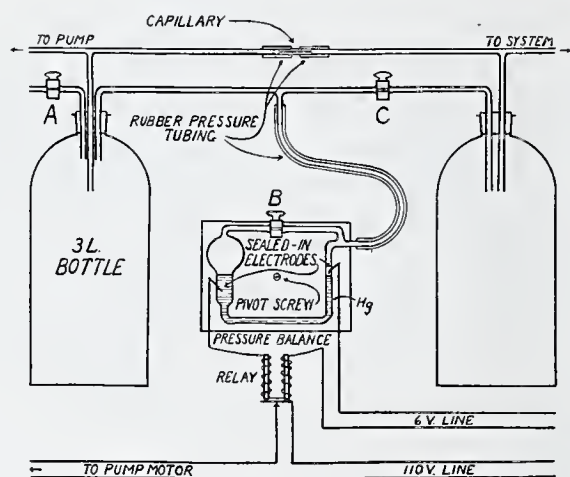


FIGURE 1. DIAGRAM OF APPARATUS

electrodes and the height to which the balance is filled with mercury are correct as illustrated. These electrodes must be gas-tight, and stopcock *B* must be kept well lubricated with a good grade of stopcock grease. The lower end of the right-hand electrode should be fairly accurately centered in the tube. The pressure balance is mounted on a board of suitable size, and the board itself supported by a screw or bolt through its center which allows it to be rotated slightly in its own plane, but which should be tight enough to prevent any accidental jarring from altering the position of the balance. Stopcock *A* should have a rather small bore; stopcock *C* should be of 3 mm. inside diameter. Glass tubing of 5 mm. inside diameter is used for making the connections between

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the contact points on the relay so that the pump motor would operate when the relay actuating circuit was completed.

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RECEIVED March 3, 1932. This work was carried out at The Johns Hopkins University, and the apparatus described was developed in connection with Research Project No. 28 of the American Petroleum Institute. The work was supported by a research fund of the Institute donated by John D. Rockefeller and administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

Determination of Olefins by Bromine Titration

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THE present procedure has been developed as a rapid method for the determination of olefins in a mixture of hydrocarbons, particularly in cracked hydrocarbon distillate. It is based upon the idea that a solution containing olefins will absorb bromine in proportion to the olefin concentration. This idea is, of course, not new; it is the factor which governs the determination of the bromine number. Instances of direct bromine titration also appear in the literature. A chloroform solution of ice-cold nerol (4) has been so titrated, bromine entering both double bonds quantitatively. The degree of unsaturation of ethyl stilbene (5) has been determined in like manner. Similarly, Kurt Meyer (3) titrated a keto-enol mixture (methyloxaloacetate) for the determination of the enol portion. Although the application to nerol and ethyl stilbene is satisfactory, the method has potential sources of error which prevent its general adoption. The errors involved, as a result of substitution, incomplete additions, etc., have vitiated the usefulness of the bromine or iodine number as applied to cracked petroleum distillate (2).

Some of the objections are overcome when the olefin concentration of an oil is calculated from the ratio of its bromine titer to that of a standard solution containing a known concentration of known olefins. This is the basis of the present work.

PROCEDURE

The titration of the experimental standard and unknown is carried out under the same conditions of light and heat in the following manner:

The oil (2 cc. or a volume which requires 1 to 5 cc. of the bromine solution) is diluted with olefin-free naphtha to a volume of 10 cc., and a 4 per cent solution by volume of bromine in carbon tetrachloride is added from a buret, five drops (0.1 cc.) at a time, stirring after each addition. The end point of the titration is that point where a definite orange color persists for 30 seconds. This end point is one which each operator has to fix in his own mind. The titration should be carried out in diffused light, since direct sunlight causes the production of excessive hydrogen bromide.

All values of concentration in this paper are expressed in terms of volume per cent.

For the case in which the standard and unknown solution contains the same single olefin, Equation 1 is used to calculate the olefin content of the solution.

$$U = \frac{T_1}{T_2} S \quad (1)$$

where U = olefin content of solution
 S = olefin content of standard
 T_1 = titer of solution
 T_2 = titer of standard

Solutions containing various amounts of octylene in olefin-free cleaner's naphtha were titrated. Tables I and II indicate the results obtained.

TABLE I. TITRATION OF SOLUTIONS CONTAINING OCTYLENE

VOL. 12% C ₈ H ₁₆ SOLN.	VOL. BR ₂ SOLN.	VOL. BR ₂ SOLN. VOL. C ₈ H ₁₆ SOLN.
Cc.	Cc.	
10	5.1	0.51
5	2.6	0.52
4	2.2	0.55
3	1.5	0.50
2	0.98	0.49

A volume of 1 cc. gave results that were entirely too low.

TABLE II

C ₈ H ₁₆ IN SOLN.	VOL. TITRATED	VOL. BR ₂ SOLUTION USED (TITER)	VOL. BR ₂ SOLN. FOR 2 CC. OF 1% C ₈ H ₁₆
%	Cc.	Cc.	Cc.
31.84	1	2.6	0.163
22.2	2	3.7	0.166
16.7	2	2.7	0.162
11.1	2	1.9	0.171
5.55	5	2.3	0.166

The amount of bromine that can be absorbed by 2 cc. of a 1 per cent octylene solution is 0.00664 cc. This corresponds to 0.166 cc. of a 4 per cent solution. The average quantity of bromine solution actually used is 0.166 cc.

The standard may also consist of an oil which contains the same type of olefin mixture as that in the oil under investigation. Equation 1 will apply in this case also. In a concurrent paper it is shown that the olefins in cracked gasolines are probably of the same type in approximately the same relative proportion. Thus a cracked gasoline in which the olefin content has been accurately determined may be used as a standard. Results are shown in Table III.

TABLE III. COMPARISON OF BROMINE AND SULFUR MONOCHLORIDE METHODS

No.	VOL. BR ₂ SOLN. Cc.	OLEFINS	
		Br ₂ method %	S ₂ Cl ₂ method (2) %
1	6.74	29.6 standard	29.6
2	6.14	27.0	28.0
3	8.72	38.2	35.0
4	6.90	30.4	29.8
5	13.0	57.0	61.4

These analyses indicate that the distribution of various olefins (including those of various types, as well as of different molecular weights) is the same in cracked distillate from various charging stocks and operations.

Equation 1 has also been found to give good results when small concentrations of olefins are to be determined. In cases of this kind larger samples are used for analysis.

The method may also be used where the solution contains known olefins different from that contained in the standard. In this case the specific gravities and the molecular weights of the olefins must be known. If the solution contains a

mixture of olefins, the average molecular weights and specific gravities will apply. The olefin content is then calculated by use of the equation

$$U = \frac{T_1}{T_2} S \cdot \frac{(N_s M_1 D_s)}{(N_1 M_s D_1)} \quad (2)$$

M_1 , D_1 , and N_1 are the actual or average molecular weight and density of and number of olefin bonds in the olefin or mixture being determined, while M_s , D_s , and N_s are the corresponding properties of the standard olefin.

If the olefin in the standard and solution is octylene and amylene, respectively, the expression $\frac{T_1}{T_2} S$ in Equation 2 gives the concentration of amylene in the solution in terms of octylene, while the expression in the brackets is the amylene equivalency of octylene.

To test Equation 2, solutions of 2-pentene, pinene, and allyl sulfide were titrated. An octylene solution was used as a standard with the results shown in Table IV. In the process of titration of the allyl sulfide, the tetrabromide was precipitated as fine white needles. Solids were deposited from solutions of pinene (and limonene) also, but they are more or less gummy.

TABLE IV. TITRATION TO TEST EQUATION 2

OLEFIN	AMT. PRESENT	$\frac{T_1}{T_2} S$	OLEFIN EQUIV. OF OCTYLENE	OLEFIN FOUND
	%			%
Amylene	4.8	7.2	0.69	5.0
	7.0	10.9	0.69	7.5
	15.0	22.6	0.69	15.6
Pinene	2.95	5.5	0.51	2.8
	3.9	7.04	0.51	3.6
	7.4	14.7	0.51	7.5
	14.6	25.3	0.51	12.9
Allylsulfide	10.0	23.8	0.41	9.8

TABLE V. PER CENT OLEFINS IN MIXTURE

No.	OCTYLENE	LIMO- NENE	PINENE	AMY- LENE	ALLYL SULFIDE	CALCD. AS OCTY- LENE	FOUND
	%	%	%	%	%	%	%
1	4.56	4.39	13.0	12.7
2	10.18	3.67	17.2	16.8
3	17.60	5.69	28.4	28.4
4	8.33	5.0	20.5	19.8
5	9.72	..	1.23	12.1	12.1
6	6.85	..	6.28	5.32	..	26.9	28.0
7	19.34	..	3.14	2.66	..	29.3	28.4
8	3.42	..	4.61	2.66	..	16.3	16.6
9	3.42	..	3.14	2.66	5.0	25.6	24.0

The two double bonds in allyl sulfide and the two potential double bonds in pinene are thus saturated quantitatively, as they are in nerol. Under the conditions of the titration, no bromine is added to the sulfur in the allyl sulfide. This inactivity is analogous to the nonreplacement of the hydroxyl group in nerol. According to Faragher, Gruse, and Garner (1), diolefins absorb halogen very rapidly in the beginning. This was observed also in this work. For example, a pinene solution absorbed 60 per cent of the needed bromine before a yellow color appeared which persisted for 30 seconds, whereas an octylene solution of double the concentration of the pinene became yellow almost from the beginning. It is of interest to note that the cracked gasolines behave as if they contained a large concentration of polyolefins, since a considerable proportion of bromine reagent was added before a yellow color was produced.

It is sometimes useful to determine the value of a mixture of olefins in terms of a standard olefin such as octylene. To determine if interfering reactions arise, Equation 3 has been applied.

$$U_s = U_1 \frac{(N_1 D_1 M_s)}{(N_s D_s M_1)} + U_2 \frac{(N_2 D_2 M_s)}{(N_s D_s M_2)} + \dots \text{etc.}$$

$$= \frac{M_s}{N_s D_s} \left(\frac{U_1 N_1 D_1}{M_1} + \frac{U_2 N_2 D_2}{M_2} + \dots \text{etc.} \right) \quad (3)$$

where U_s is the olefin concentration in terms of the standard, and U_1 , U_2 , etc., are the concentration of the various olefins in the mixture.

The factors for amylene, pinene, limonene, and allyl sulfide in terms of octylene as the standard are calculated to be 1.44, 1.97, 1.92, and 2.43, respectively.

DETERMINATION OF OLEFINS AND TERPENES

The bromine titration method cannot be used for olefin mixtures unless the average molecular weights and specific gravities of the olefins are known. If in a simple mixture containing two known olefins one of the olefins may be removed, however, the concentration of each olefin can be determined by this means. Mixtures of octylene and limonene were analyzed by titrating the oils before and after removal of most of the limonene.

The limonene was separated from the octylene by selective polymerization. The reagents tried were metallic sodium and the following acids: nitric, phosphoric, phosphorous, mono-, di-, and trichloroacetic, and sulfuric. All except the last polymerized limonene to a limited extent only. Table VI shows the proportions of the terpene remaining in the oil after a 9.36 per cent solution of limonene in olefin-free cleaner's naphtha was treated with the various reagents and distilled to the original end point. Phosphoric, phosphorous, and the chloroacetic acids polymerized only 30 per cent of the limonene as determined by bromine titration (the original solution being used as a standard) or by observation of the refraction of the distillate.

TABLE VI. TERPENE IN OIL AFTER TREATMENT

REAGENT	REFRACTIVE INDEX OF DISTILLATE	LIMONENE POLYMERIZED
		%
49% HNO ₃	1.4157	87
89% H ₃ PO ₄	1.4179	27
H ₃ PO ₃	1.4179	23
ClCH ₂ CO ₂ H	1.4176	..
Cl ₂ CHCO ₂ H	1.4179	..
Cl ₃ C.CO ₂ H	1.4167	(terpineol formation noted)

Sulfuric acid gave much better results. The best results were obtained as follows: The oil was shaken with three-tenths its volume of sulfuric acid of 80 per cent concentration for 30 minutes, allowed to stand for 1 hour, the acid layer withdrawn, and the oil distilled to the original end point. The distillate from the treatment of the limonene solution retained an olefin content equivalent to 7 per cent of the limonene in the untreated oil. This residual olefin is not limonene, since it is not further reacted upon by retreatment, but for the sake of calculation it may be so considered.

Under the same conditions 11.0 per cent of octylene is removed. That the relative proportion of octylene remaining after treatment is almost independent of the octylene concentration is shown in Table VII.

TABLE VII. EFFECT OF OCTYLENE CONCENTRATION

CONCENTRATED OCTYLENE Before treatment	OCTYLENE After treatment	OCTYLENE UNAFFECTED
%	%	%
5.17	4.63	89.5
5.26	4.68	89.0
12.25	10.5	86.0
15.67	13.82	88.2
22.8	20.75	91.0

The average proportion of the octylene remaining after treatment is 89 per cent.

According to Equation 3, the olefin concentration, M , of a mixture of octylene and limonene in terms of octylene is given by the expression

$$M = E + 1.92 L \quad (4)$$

where E and L are the volume percentages of octylene and limonene, respectively.

TABLE VIII. ANALYSIS OF MIXTURES FROM TABLE V

MIXTURE %	M	D	OLEFIN FOUND %
4.56 octylene	12.7	4.6	4.7 octylene
4.39 limonene			4.2 limonene
10.18 octylene	16.8	9.6	10.3 octylene
3.67 limonene			3.4 limonene
17.60 octylene	28.4	16.1	17.3 octylene
5.69 limonene			5.8 limonene

As already stated, a solution containing octylene and limonene, upon treatment with sulfuric acid under the specific conditions given, results in a distillate containing the equivalent of 7 per cent of the limonene and 89 per cent of the octylene added. The olefin content, D , in terms of octylene is then

$$D = 0.89 E + (0.07 \times 1.92) L \quad (5)$$

By the simultaneous solution of Equations 4 and 5, the values of E and L are obtained.

$$L = 0.56 M - 0.63 D \quad (6)$$

$$E = M - 1.92 L \quad (7)$$

Mixtures 1, 2, and 3, Table V, were analyzed with satisfactory results, shown in Table VIII.

The method can be applied to pinene and linalool, and probably to other terpenes and terpene alcohols. However, it is very limited in its scope as, for example, trimethyl ethylene is wholly polymerized and 3-methylcyclohexene is two-thirds polymerized.

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Approximate Determination of Olefin and Aromatic Hydrocarbons

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A METHOD has been described for the determination of olefin and aromatic hydrocarbons (2) in cracked gasolines involving the determination of the sum of the concentration of these hydrocarbons, the removal of the olefins by means of sulfur monochloride and distillation from the reaction products, and finally, the determination of the aromatic hydrocarbons in the olefin-free oil. Where the work is of such nature that an absolute error of 1 to 3 per cent is acceptable, the time may be shortened considerably by the use of the method described herein.

The sum of the olefins and aromatic hydrocarbons is determined in a manner in which the technic is modified slightly from that described in the previous article. The olefin concentration may then be calculated from the weight of residue remaining after distillation of the oil obtained upon treatment with 91 per cent sulfuric acid by the use of empirical formulas developed in this work.

Obviously, the aromatic hydrocarbon content constitutes the difference between the total volume per cent of olefin and aromatic hydrocarbons and the olefin concentration.

All values of concentration in this work are expressed in terms of volume per cent.

DETERMINATION OF TOTAL OLEFIN-AROMATIC HYDROCARBON CONTENT

The oil (100 cc.), measured in a weighed graduate, is shaken with 3 volumes of 91 per cent sulfuric acid for 30 minutes in a 500-cc. separatory funnel. The mixture is allowed to settle for 30 minutes, the acid layer withdrawn, and the oil permitted to stand 30 minutes longer, any sludge accumulating being withdrawn in the meantime. The stopcock and stem of the separatory funnel are also freed from sludge. The oil is transferred directly into a weighed 200-cc. short-neck round-bottom flask, from which the oil is distilled to a temperature 5° above the end point of the original oil, as previously determined in a similar manner. The flask is provided with a small uninsulated Hempel column (effective size 3 by 0.5 inches). The weighed graduate is used as a receiver.

The distillation loss may be determined from the weight loss and the density. If the distillation is carried out with

ice in the condenser and with the receiver in an ice-water bath, the loss may be assumed to be 1 cc., which is the average loss sustained in the many distillations made in this work. The distillate is transferred to the same funnel used for the 91 per cent sulfuric acid treatment, and treated with 3 volumes of 98 per cent sulfuric acid in the manner described above. The treated oil is measured and weighed in the graduate used heretofore, and its specific gravity calculated. The total volume per cent of olefins and aromatic hydrocarbons is calculated according to the formula

$$S = V_1 - (V_2 + l) \quad (1)$$

where V_1 is the volume of the original oil, V_2 the volume of oil remaining after the second acid treatment, and l the average distillation loss. The following equations showing the relationship between the weight of the distillation residue and olefin content were developed empirically:

A: For gasolines with a $\frac{P}{D}$ factor of 10 to 25 (15 to 35 per cent olefin content)

$$U = 1.3 \frac{P}{D} \quad (2)$$

or
$$U = \frac{P}{D} + 6 \quad (3)$$

B: For gasolines with a $\frac{P}{D}$ factor of 25 to 35 (35 to 50 per cent olefin content)

$$U = 1.4 \frac{P}{D} \quad (4)$$

or
$$U = \frac{P}{D} + 13 \quad (5)$$

C: For gasolines with a $\frac{P}{D}$ factor of 35 to 40 (50 to 60 per cent olefin content)

$$U = 1.5 \frac{P}{D} \quad (6)$$

or
$$U = \frac{P}{D} + L + 15 \quad (7)$$

where P is the weight of the distillation residue, L the loss in volume per cent sustained on the treatment with 98 per cent sulfuric acid subsequent to distillation, and D the density of the oil remaining after the 98 per cent acid treatment.

As applied to the present work, Group A corresponds roughly to gasolines produced by cracking processes operating at temperatures of 400–480° C., Group B at temperatures of 480–510° C., and Group C at temperatures of 510–570° C. The temperature relationship may be highly limited, as the time-temperature factor is controlling in this respect.

For use of Formula 7, the volume of distillate at room temperature must be known in order to determine L . Otherwise, even this reading need not be considered. The volume of oil, V_T , at room temperature, T , may be calculated from the observed volume, V , and the observed temperature of the distillate, t , according to the formula

$$V_T = V \left(1 + \frac{T - t}{1000} \right) \quad (8)$$

Several cracked distillates were analyzed using the more accurate method previously referred to (sulfur monochloride), and the results were compared with those determined by the present method using Equations 2 to 7, inclusive. These results are shown in Tables I, II, and III.

TABLE I. ANALYSIS OF DISTILLATES ACCORDING TO GROUP A

ANALYSIS	CRACKED DISTILLATE	OLEFIN CONTENT		
		Observed	Calculated	
		(S ₂ Cl ₂ method)	Eq. 2	Eq. 3
		%	%	%
1	California	21.4	22	22
2	Panhandle	32.8	34	32
3	Seminole	29.1	26	26
4	Pennsylvania	25.5	25	25
5	Venezuela	20.6	20	22
6	West Texas (Pecos)	32.8	32	30
7	Mexican (Panuco)	27.3	28	27
8	Smackover	31.1	32	30
9	Pennsylvania	28.0	27	26
10	Pennsylvania	28.7	29	28
11	Midcontinent	30.9	28	27
12	Midcontinent	29.8	27	26

An overhead distillate, boiling range 210° to 258° C., from a Midcontinent pressure distillate was analyzed. It contained 16.2 per cent olefins according to the sulfur chloride method, and gave 17 and 19 per cent, respectively, for the olefin content, according to Equations 2 and 3.

TABLE II. ANALYSIS OF DISTILLATES ACCORDING TO GROUP B

ANALYSIS	CRACKED DISTILLATE	OLEFIN CONTENT		
		Observed	Calculated	
		(S ₂ Cl ₂ method)	Eq. 4	Eq. 5
		%	%	%
1	Midcontinent kerosene	44.4	45	45
2	Pennsylvania kerosene	48.3	52	50
3	Pennsylvania fuel oil	47.9	45	45

A preliminary test indicates that oil obtained by polymerizing ethylene falls in Group B.

TABLE III. ANALYSIS OF DISTILLATES ACCORDING TO GROUP C

ANALYSIS	METHOD	OLEFIN CONTENT		
		Observed	Calculated	
		(S ₂ Cl ₂ method)	Eq. 6	Eq. 7
		%	%	%
1	Laboratory experimental	60.1	59	61
2	Semi-commercial experimental	59.1	58	59
3	Commercial A	60.6	62	61
4	Commercial B	61.4	65	61

Equation 7 gives better results than Equation 6.

DISCUSSION

It should be stressed that the formulas given for the calculation of the olefin content are purely empirical. Whereas the olefin-residue ratio for Group A gasolines shown in Table I is about 1.3, that of octylene in the presence of aromatic hydrocarbons is only 1.0. This is probably due

to a portion of the latter appearing as condensation products with octylene, balancing the portion of octylene dissolved in the acid. On the other hand, the ratio for amylene is very high, 2.5, indicating great solubility of the olefin in the acid. This value decreases to 1.4 when aromatic hydrocarbons are also present.

It is interesting to note that olefin-residue ratios may vary with the boiling range of gasoline. For a Group A gasoline, the fractions boiling within the ranges 64° to 95°, 95° to 125°, 125° to 150°, and 150° to 180° C., the ratios are 1.4, 1.2, 0.93, and 0.94, respectively. For the fractions of a Group C gasoline boiling between 60° to 95°, 95° to 125°, 125° to 150°, 150° to 175°, 175° to 200°, and 200° C. to the end point, the ratios were 1.4, 1.2, 1.2, 1.2, 1.6, and 2.0. Removal of a part of the olefins, as may be done by treatment with 80 per cent sulfuric acid, changes the ratio from 1.3 to 1.1. This result clearly shows the effect of the absence of the olefins that are readily soluble in the acid.

OLEFIN-RESIDUE RATIO

As has been stated in the literature (1), several types of reaction take place between sulfuric acid and olefins—namely, esterification, alcohol formation, oxidation, polymerization, and condensation with aromatic hydrocarbons when the latter are present. Another complex reaction takes place in which the products are saturated hydrocarbons (3, 4, 5). To what extent each of these types of reaction occurs depends chiefly upon the concentration of acid used and the nature of the olefin. Therefore, when an oil is treated with 91 per cent sulfuric acid, the concentration of products remaining in the oil and appearing as residue upon distillation—i. e., the polymerized products—is a function of the type of olefins.

Examination of the analyses has shown that the ratio between the olefin content of a gasoline obtained from a cracked distillate and the distillation residue in these analyses is fairly constant. This shows that regardless of the source and composition of the charging stock, the mixture of the olefins formed upon cracking consisted of the same types in the same relative proportions. The calculation showed, therefore, that for Group A three-quarters of the olefins originally present in the gasoline are found in the residue as reaction products. The constancy of the olefin-residue ratio (U to P/D) seems to hold for distillates obtained from various charging stocks and methods of processing, and depends principally on the operating conditions, particularly the time-temperature history, of the cracking operation. Other factors being equal, increase in cracking temperatures produces gasolines with increased olefin-residue ratios. Hence, not only is the total olefin content greatly increased, but the ratio of acid soluble to total olefins is also increased. This increased solubility is an indication of the presence of the more reactive olefins, and thus of the gum-forming constituents. In some types of gasoline the olefin-residue ratio may also bear a relationship to the antiknock properties of the gasoline which increase with this ratio. As a consequence, the antiknock value and gum content should increase at a greater rate than the olefin content.

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Automatic Apparatus for Intermittent Washing

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THE device here described was developed for washing experimental photographic emulsions, but it may be of value in other cases where the interchange between the solvent and the product is slow and the solvent must be utilized efficiently.

A photographic emulsion is normally prepared by precipitation of the silver halide in the presence of gelatin; after digestion to "ripen" the product, the emulsion is chilled until the gelatin sets to a firm jelly, then cut into shreds or "noodles" and washed to remove the by-products of the reaction and the soluble bromide which is invariably present in excess. For mechanical reasons, the shreds must be at least a few millimeters thick, so that the diffusion of soluble salts out into the wash water takes much longer than from the thin layer of emulsion on a finished plate or film.

In commercial practice emulsions are washed in running tap water, preferably from deep wells for uniformity, and prefer-

ably containing some hardness to reduce swelling of the gelatin. For certain experimental work the use of distilled water, plus a small amount of magnesium sulfate, became desirable for reproducibility. As the batches of emulsion had an initial volume of 1.0 to 1.2 liters, from which 10 grams of ammonium bromide plus other salts were to be removed quite completely, the expenditure of distilled water would be at best very considerable.

The apparatus now in use is shown in vertical section in Figure 1, and the wiring diagram for the clock control is indicated in Figure 2. The emulsion is held in a nickel wire-screen basket in the tank *A* (made by cutting the bottom off a 3-gallon bottle). The wash water enters and leaves through a two-way stopcock, *B*, of 4-mm. bore, connected to the bottle neck. The amount of water supplied for each change by siphon from a tank is regulated by the float valve *C*, which is of the general design suggested by Othmer (*1*), but with a glass needle to close the inlet hole in a rubber stopper. The valve and float assembly may be slid up and down in the float chamber to regulate the height of water in *A*. The distinctive feature of the apparatus is the use of the stock two-way cock, turned by a small motor which can be controlled directly by clock contacts. The motor, *D* ($\frac{1}{100}$ h. p., 110 volt, 60 cycle, a. c. series wound), drives the stopcock through a worm gear and belt. On the driven shaft, between the driven pulley and the clamp attached to the stopcock key, there are three slip rings. Brushes supported by the same cross strut as the shaft bearings make contact on these as indicated in the wiring diagram, Figure 2. One ring is split in half; each segment is connected with one of the other rings. The clock contacts are alternately connected to the other two rings. When contact is made at the clock, the motor is energized and rotates the shaft 180 degrees. The brush on the split ring is allowed to bridge the gap so that as soon as contact with one half is broken, the circuit is ready to be completed through the other half and the corresponding clock contact.

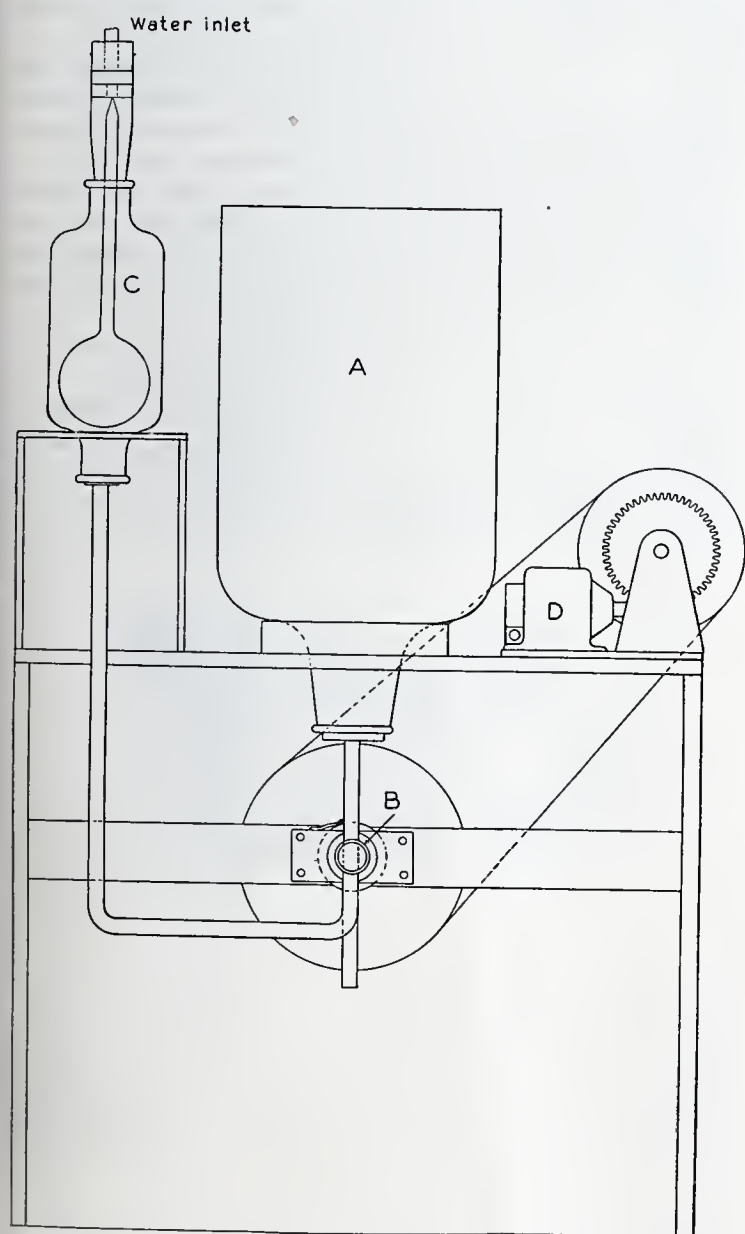


FIGURE 1. AUTOMATIC WASHING DEVICE FOR PHOTOGRAPHIC EMULSION

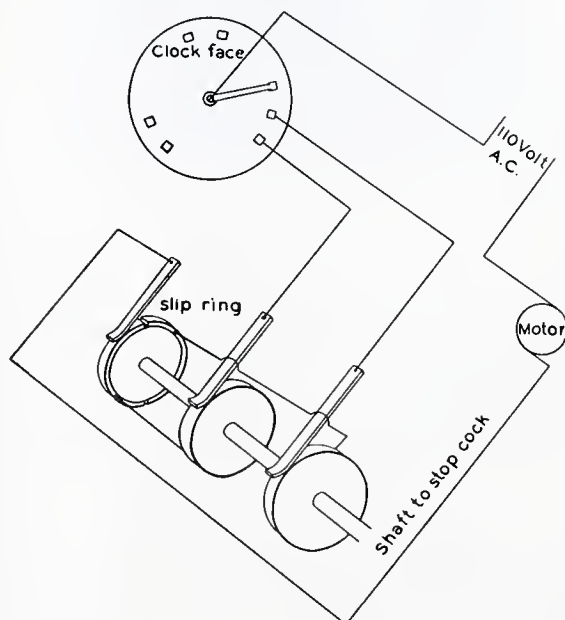


FIGURE 2. WIRING DIAGRAM FOR EMULSION-WASHING DEVICE

The shop work involved in construction of the apparatus was no greater than would be required for construction of solenoid valves, and no relays or heavy currents are necessary. The apparatus now runs on a 20-minute cycle, allowing 3 minutes for draining, but it may obviously be adopted to any other timing where the intervals are not too short. Batches of emulsion of 1.2 liters initial volume can be washed to a bromide-ion concentration of $1 \times 10^{-4} N$ with an expenditure of 60 to 75 liters of water (6 to 7 hours at 5° to 10° C.).

The water is used more efficiently than by an intermittent

siphon device, since the emulsion is completely covered within a minute after the cock is turned to the inlet position. Provision might obviously be made for stirring the material in the tank; it has been omitted for these relatively small batches of emulsion because the jelly is easily broken up by handling.

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Device for Removing "Frozen" Plugs from Stopcocks

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THE successful removal of a "frozen" stopcock plug has frequently resulted in saving valuable apparatus and time. The gain accruing from this simple operation has tempted many chemists to delve somewhat into this, and almost every laboratory has constructed at least one stopcock key remover. At present, several forms are commercially available from apparatus companies. Although some of these efforts are ingenious and to a degree successful, they possess as a group one distinct disadvantage and one severe

be used in all cases where the stopcock is accessible, and in addition will serve in places not easily reached in a mounted apparatus where the stopcock is placed with the longitudinal axis of the barrel perpendicular to the plane of the apparatus front. The clamp type (Figure 2) is designed specifically to overcome the limitation of inaccessibility, and is particularly applicable when the remover must be brought to the stopcock. When the cock is sealed into a mounted apparatus so that the longitudinal axis is parallel to the apparatus front (a preferable technic of assembly, especially with oblique bored cocks), the clamp model may be used in places where no other device will enter. It requires a space equal to the width of the end collars—i. e., only several millimeters. From practical considerations, then, it may be expected to enter any space that the stopcock itself occupies.

The device shown in Figure 1 is constructed with jaws (A-A) which are hinged at the points marked 1 and 2, and are adjusted by the knurled nut B to accommodate stopcock barrels of various sizes. Pressure is applied to the stopcock plug by jack screw C, which is threaded $\frac{3}{8}$ S. A. E. Nut B is threaded $\frac{5}{8}$ S. A. E. and turns on a barrel which is threaded both inside and out. The inside thread fits the jack screw. A fiber plug is inserted in the end of the jack screw and small pieces of adhesive tape are placed in position, as illustrated, to prevent the glass from coming in contact with the steel. This device is very easily handled and will remove the most stubbornly frozen stopcock plug.

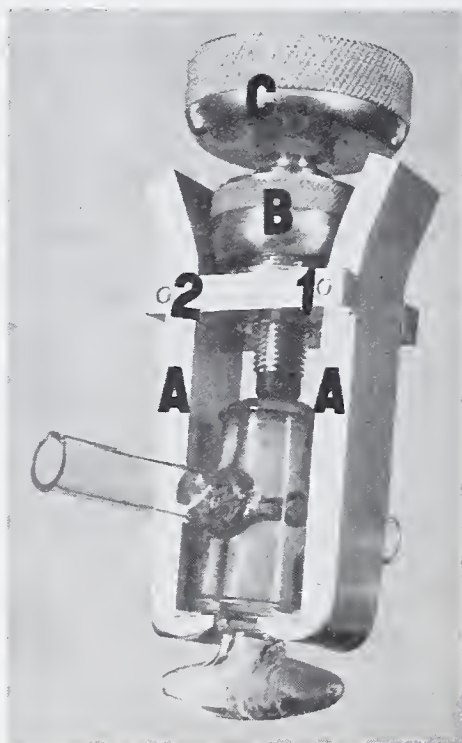


FIGURE 1. WHEEL-PULLER TYPE

limitation: the lack of quick adaptability to a stopcock of a particular size, which may happen to be any of a wide range of sizes; and the frequent impossibility of applying the remover to stopcocks located in difficultly accessible places. This will occur when the stopcock is sealed into a permanently mounted apparatus which may be so complicated or compact as to prevent the actual placement of the remover around the stopcock.

The two key removers described, designed to eliminate these undesirable features, possess certain features which, so far as known, are novel. The "wheel-puller" model (Figure 1) is constructed with adjustable jaws which will accommodate stopcocks of any size without recourse to one of a set of fixed spacers, receptacles, or collars. It is quickly adaptable, may



FIGURE 2. CLAMP TYPE

Figure 2 illustrates the clamp type of plug remover. At point D a fiber plug is fitted to bear on the small end of the stopcock plug. The opposing jaw is counter-bored to fit a Bakelite ring which is machined to bear on the stopcock barrel. Parts marked E are Bakelite rings, one larger and one smaller than the one in use on the apparatus in the illustration. It was found that three rings would be enough to cover the range of stopcock sizes in general use in these laboratories.

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Impurities in White Sugars

V. Determination of Phosphorus and Silica

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FURTHER work with the adaptation to white sugars of the Briggs-Bell-Doisey method for determining phosphorus (1) revealed the fact that the method for total or organic phosphates gives consistent results only on duplicate determinations which are carried out simultaneously. A short time after the publication of this method, Pincussen et al. (5) described a very similar one for the determination of small quantities of silica after phosphates have been precipitated from the solution as ammonium magnesium phosphate. Oberhauser and Schormüller (4) have described a ceruleomolybdate method for determining silica which differs from the authors' and from Pincussen's in that the color is developed in alkaline solution by sodium stannite. They state that phosphates and arsenates interfere in this method by giving the same color as the silicates. They point out, however, that in accurate work there is no danger of error in identity, since, after the silica has been removed completely by dehydration with concentrated hydrochloric acid, the phosphates and arsenates may be detected in the filtrate.

Isaacs (3) has described another ceruleomolybdate technic for silica which was critically examined by Foulger (2). The latter, in concluding his report, states: "The fact that both silicon and phosphorus can be estimated by the color produced on reduction of their molybdates would suggest that the results for the phosphorus content of tissues obtained by this method are actually estimations of phosphorus plus silicon. We have experimental evidence that some procedures for estimation of phosphorus by reduction of the phosphomolybdate can be used equally well for the estimation of silicon. This question is worthy of a separate investigation. We are undertaking further research on this point and on the whole mechanism of the reduction of molybdates." So far as the authors are aware, this is the only reference to a ceruleomolybdate method for the determination of silica and of phosphorus together, and no further report of the investigation mentioned by Foulger has been made.

It seemed probable that the difficulty in our method was caused by incomplete reaction of the silica in the sugar with the sodium carbonate with which the sample is ashed. In the case of simultaneous duplicates, each receives the most accurately controlled duplication of conditions of temperature, length of time of incineration, and details of manipulation possible. If the duplicates are not carried on simultaneously, the conditions and technic cannot be so accurately duplicated, and consequently varying quantities of the silica react with the carbonate. A critical study of the procedure has confirmed this supposition and has led to the development of the method so that it is possible to determine both the silica and the phosphorus. The only other known

Irregularities in the results obtained by the authors' method for determining phosphorus in white sugars have been found to be due to the interference of silica. The ceruleomolybdate method, by means of a definite technic, may be used to determine total phosphates plus silica. After removal of the silica by dehydration with nitric acid, the total phosphates may be determined colorimetrically in the filtrate. The difference of the values found in the two determinations represents the silica. Inorganic phosphates may be determined directly on solutions of the sugar. The silica present in white sugars is in a combination which does not react in the ceruleomolybdate method until after the ash has been fused with alkali carbonates.

interference is the possible presence of arsenic in the sugars. Although this seemed hardly probable, it could not be completely ignored in view of the wide occurrence of small amounts of arsenic in manufactured products. The ash from 20-gram portions of sugar was prepared and fused by the method given below and tested for arsenic by the Gutzeit procedure. No arsenic in excess of the quantity present in the reagents was detected. If arsenic should be present in the sugar, it would render the values for P_2O_5 inaccurate, but would not affect those for silica.

REAGENTS

MOLYBDATE SOLUTION. Twenty-five grams of ammonium molybdate are dissolved in 300 cc. of water and to this are added 200 cc. of water containing 75 cc. of concentrated sulfuric acid.

HYDROQUINONE SOLUTION. Half a gram of hydroquinone is dissolved in 100 cc. of water to which a drop of sulfuric acid has been added to retard oxidation.

SULFITE SOLUTION. Twenty grams of sodium sulfite are dissolved in 100 cc. of water. The solution should be freshly prepared.

MIXED ANHYDROUS CARBONATES. Equal parts of pure anhydrous sodium and potassium carbonates are intimately mixed and kept stoppered as a stock reagent.

CONCENTRATED NITRIC ACID. Sp. gr. 1.42.

ACETIC ACID SOLUTION. Twenty per cent by volume.

STANDARD PHOSPHATE SOLUTION. A sample of potassium dihydrogen phosphate weighing 0.4394 gram is dissolved in water and diluted to 1 liter. Twenty-five cubic centimeters of this solution are then diluted to 200 cc. This gives a solution which contains 0.0287 mg. of P_2O_5 per cc.

STANDARD SILICATE SOLUTION. The percentage of SiO_2 in a solution of water glass is determined gravimetrically. A portion of the water glass solution sufficient to contain 0.725 gram of SiO_2 is weighed out and diluted with distilled water to 1 liter. Five cubic centimeters of this solution are diluted to 100 cc. with distilled water. Both of these silica solutions must be made fresh on the day they are to be used, since on standing the silicate hydrolyzes to silicic acid, which becomes colloidal and nonreactive. The solution of water glass from which these solutions are made should be limpid, and should be taken from a previously unopened bottle. The dilute solution contains 0.0363 mg. of SiO_2 per cc. and is equivalent to the standard phosphate solution (Tables I and II).

TABLE I. EQUIVALENCY OF SiO_2 AND P_2O_5 SOLUTIONS

(1 cc. of SiO_2 solution contains 0.0363 mg. of SiO_2 ; 1 cc. of P_2O_5 contains 0.0287 mg. of P_2O_5)

SiO_2 SOLN. TAKEN	P_2O_5 SOLN. TAKEN	EQUIVALENT TO P_2O_5 SOLN.		
Cc.	Cc.	Cc.	Cc.	Cc.
0.0	0.0	0.0	0.0	
0.5	0.0	0.5	0.5	
1.0	0.0	1.0	1.1	1.0
1.5	0.0	1.5	1.5	
2.0	0.0	2.0	2.1	1.9
2.5	0.0	2.9	2.5	
3.0	0.0	3.2	2.9	2.9
3.5	0.0	3.5	3.4	
4.0	0.0	3.7	3.5	
0.5	0.5	1.0		
1.0	1.0	2.0		
1.5	1.5	3.1		
2.0	2.0	4.0		

TABLE II. RECOVERY OF SiO₂ AND P₂O₅

SiO ₂ SOLN. TAKEN	P ₂ O ₅ SOLN. TAKEN	SiO ₂ ^a STD. SOLN. FOUND		P ₂ O ₅ STD. SOLN. FOUND	
Cc.	Cc.	Cc.	Cc.	Cc.	Cc.
A. NO SUGAR USED					
0.0	0.5	0.6	0.4
0.0	1.0	1.2	0.8
0.0	1.5	1.6	1.4
0.0	2.0	2.2	2.0
0.5	0.0	0.6	0.5
1.0	0.0	1.2	1.0
1.5	0.0	1.5	1.6
2.0	0.0	1.9	2.0
B. ADDED TO SUGAR "A"					
0.0	1.0	-0.1		1.0	
0.0	2.0	0.0		2.0	
0.0	3.0	0.0		3.0	
1.0	0.0	0.9		0.0	
1.0	1.0	1.1		0.9	
1.0	2.0	1.1	1.2	1.9	1.9
1.0	3.0	1.0		2.9	
2.0	0.0	1.9	1.8	0.1	0.1
2.0	1.0	2.0		1.0	
2.0	2.0	1.9		2.0	
3.0	0.0	2.8		0.0	
3.0	1.0	2.8		1.0	

^a Measured against P₂O₅ standards.

PREPARATION OF COLORIMETRIC STANDARDS. The standards for the colorimetric comparison are developed simultaneously with the unknowns. Since the silica standard is equivalent to the phosphate standard, only the latter need be used in analyses, which obviates the uncertainty liable to be encountered concerning possible deterioration of the silica standard and also saves time and expense. Measured volumes ranging from 0.1 to 4.0 cc. of the standard phosphate solution are placed in 100-cc. Nessler tubes. To each are added, in the order given, 5 cc. of the molybdate solution, 1 cc. of the sulfite solution, 1 cc. of the hydroquinone solution, and enough distilled water to make a final volume of 100 cc. The solutions are mixed and allowed to stand for 30 minutes. Standard solutions made up with and without the addition of pure sucrose showed no difference in hue or depth of the colors developed.

PROCEDURE

P₂O₅ PLUS SiO₂. Five grams of sugar were mixed with 0.2 gram of the anhydrous mixed carbonates in a platinum dish which just previously had been thoroughly cleaned by fusion of a considerable quantity of the carbonates. When the mixture had been reduced to a white ash by careful charring followed by incineration at 550° C. in an electric muffle, the residue was fused over a free flame to a clear liquid melt. After the melt had cooled it was dissolved in about 15 cc. of cold distilled water, acidified with 1 cc. of the dilute acetic acid (which just neutralizes the carbonates), and transferred without filtering to a 100-cc. Nessler tube. The color was developed by the addition of the molybdate, sulfite, and hydroquinone solutions as described above, and after 30 minutes was compared colorimetrically with standards which were developed simultaneously from the standard phosphate solution. Iron in the sugars causes a yellowish tinge, which is conveniently equalized by viewing both the standards and the unknown through a yellow Wratten light filter (K-3 No. 9). The result was recorded as the number of cubic centimeters of the standard solution which matches the unknown and was corrected for the amount of P₂O₅ plus SiO₂ found in the reagents in a blank determination.

TOTAL P₂O₅. Five grams of the sugar were ashed with 0.2 gram of the mixed carbonates as in the preceding determination, but the ash was not fused. After it had cooled it was dissolved in a little water and acidified with concentrated nitric acid. The silica was rendered insoluble by evaporating the solution to dryness on the steam bath, moistening the residue thoroughly with concentrated nitric acid, again evaporating to dryness, and taking up in a little water (6). The solution was immediately filtered to remove the separated silica, and the filtrate and washings were collected together in a 100-cc. Nessler tube. The color was developed and measured as before, similarly recorded, and corrected for the

total P₂O₅ found in the reagents in a determination made on them alone. A series of experiments involving various modifications of technic showed that this method of removing the silica was both simple and sufficiently accurate for this work (Table II).

INORGANIC P₂O₅. Ten grams of the sugar were dissolved in a little water in a Nessler tube. To this the molybdate, sulfite, and hydroquinone solutions were added, the colors developed, measured, and corrected for inorganic P₂O₅ in the reagents, and the results recorded as described above.

CALCULATION OF RESULTS

SiO₂. The value obtained in the determination of total P₂O₅ was subtracted from that obtained in the determination of SiO₂ plus P₂O₅ and the result multiplied by 0.0363. This gave the weight of SiO₂ in milligrams, from which the parts per million were obtained by multiplying by 200.

ORGANIC P₂O₅. One-half the value obtained for the inorganic P₂O₅ was subtracted from that obtained for the total P₂O₅ and the result multiplied by 0.0287. This product multiplied by 200 gave the parts per million.

INORGANIC P₂O₅. The corrected value found for inorganic P₂O₅ was multiplied by 0.0287 and again by 100 to obtain the parts per million.

DISCUSSION

This ceruleomolybdate procedure for silica is much more sensitive to changes in hydrogen-ion concentration than the one for phosphates. If the solution in which the determination of silica is to be made is strongly acid, the color develops very slowly, and only very pale shades are obtained. If, however, the original solution is alkaline, the color develops very rapidly and becomes very intense. Attempts to neutralize the fused carbonates with nitric acid showed that the establishment of neutrality with this acid was not practicable, since the least excess caused irregularities probably due not only to a lowering of the pH, but also to some extent to a partial transformation of the silicate ions into complex polysilicate ions whereby some of the SiO₂ is rendered inactive. Acetic acid, however, added in the stoichiometric amount necessary for neutralization (0.2 gram per 0.2 gram of mixed carbonates) gives a buffered solution of lower hydrogen-ion concentration in which the blue color due to silica develops at such a rate that at the end of 30 minutes it is comparable to that due to the phosphates when the technic described in the preceding paragraphs is adhered to. Any divergence from this technic requires the determination and use of a different equivalent value for SiO₂ in relation to P₂O₅.

Because of the depth of the color produced, it is almost impossible to make accurate comparisons with the naked eye (or with the color filter) if the solutions contain more P₂O₅ plus SiO₂ (or either) than is equivalent to a total of 4 cc. of the standard phosphate solution. If larger amounts are encountered, the determination may be repeated on a smaller sample of the sugar, or suitable aliquots of the darker solution may be diluted to 100 cc. before the comparison is made.

The method is subject to errors of 0.1 and 0.2 cc. of standard solution in the determinations of phosphates and of silica, respectively, as is shown by the results which are recorded in Table II-B and which were obtained by adding known volumes of the standard solutions of phosphate or silica, or both, to sugar "A" and carrying out the procedures described. Calculated on the basis of 5 grams as the weight of the samples taken, these errors are 0.57 and 1.5 parts per million for P₂O₅ and SiO₂, respectively. By using larger samples of the sugar for the ashing, the errors calculated to

parts per million may be proportionately decreased. However, the use of a larger original sample for the P_2O_5 plus SiO_2 is not feasible, since in most cases it would make the quantity of SiO_2 greater than that which may be measured accurately by this technic. If only the total P_2O_5 is to be determined, this limitation does not hold, and in general weights of sample up to 15 grams may be used.

TABLE III. SiO_2 AND P_2O_5 IN WHITE SUGARS

SAMPLE	SiO_2 P. p. m.	ORGANIC P_2O_5 P. p. m.	INORGANIC P_2O_5 P. p. m.
a	8.7	0.0	0.0
b	29.0	0.8	0.3
c	21.8	1.1	Trace
d	45.1	1.1	Trace
e	38.5	0.5	0.1
f	9.4	0.6	Trace
g	8.0	0.6	Trace
h	53.0	0.3	0.3
i	29.0	1.1	Trace
j	52.3	1.1	0.0

The values for organic P_2O_5 recorded in the previous article (1) are incorrect in that they include a part of the SiO_2 as well as the actual organic phosphorus. Unfortunately the samples of the sugars on which those analyses were made have been exhausted, and therefore the correct values cannot be given. Table III gives the values found in more recent sugar samples representing both refined and direct-consumption cane sugars, as well as beet sugars. It is to be noted that the quantity of SiO_2 greatly exceeds that of the organic phosphates.

The results indicate that the silica in the sugars is in a nonreactive form, since it does not give the reaction until after it has been made soluble by carbonate fusion, as shown in those cases which contain silica but which give no test for inorganic phosphates. The extreme ease with which

the silicate ions pass into nonreactive complexes is shown by the impossibility of preserving the standard silicate solutions and by the following experiment which was performed in triplicate: A solution of water glass containing 0.109 mg. of reactive silica was added to 10 grams of sugar "A" and heated in a vacuum oven at 70° C. for 24 hours. After the lumps had been broken up, the sugar was allowed to stand in the open air for 7 days. A determination by the procedure for inorganic phosphates showed no more color than that developed in the blank on the reagents. Since by this simple treatment the silica was rendered non-reactive, there is no reason to suppose that silica in the juices will remain in the active form throughout the more vigorous treatments used in the processes of manufacturing white sugar.

ACKNOWLEDGMENT

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A Convenient Feed Cup for Rats

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THE feed cup described by McCollum (1) is a useful device for feed conservation in nutrition studies. Frequently, however, the materials available locally for its construction are of such proportions that the cup occupies considerable space within the cage and requires an excessive amount of feed to fill it. Large amounts of feed are consequently lost during periodic renewal of the ration.

A feed cup constructed entirely from tin cans has been devised for use in this laboratory. Its construction is quite simple, as the accompanying photograph indicates. Two cans of closely similar diameters are chosen so that one will readily fit within the other without binding. The cans are cut to approximately the same height on a lathe or by means of tin shears. A round hole is then made in the end of the inner can by a lathe or round tinner's punch. The hole should be of sufficient size to permit easy entrance of the animal's head. Diameters of 1, 1.125, and 1.25 inches have been found to be the most useful sizes.

When the larger can is

filled with feed and the smaller forced down into position, the rat must reach through the hole in order to consume the ration. The cup appearing in the photograph was constructed from cans of $2\frac{11}{16}$ and $2\frac{8}{16}$ inches in diameter. The hole in the end of the inner can is 1 inch in diameter.

The cup may be suspended from the top of the cage by wires or permanently attached to the side. In the latter case it will be found that, by fastening the cup to the cage at a decided angle, the possibility of excreta lodging in the cup as a result of the animal perching upon it will be greatly reduced.

The device is compact and easily manipulated and cleaned. Many standard can sizes are available, making possible the construction of a number of different sized feed containers.



COMPONENT PARTS SHOWING METHOD OF ASSEMBLY AND SUSPENSION

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RECEIVED February 15, 1932.

Effect of Inerts on Coking Properties of Pittsburgh Bed Coal

Determination by Small-Scale Carbonization Test

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IN A previous publication (2) the effect of inerts on the coking power of Pittsburgh coal was studied. The Marshall-Bird method for determining agglutinating power was used to measure the effect, and it was found by this method of investigation that the addition of fine inert material, such as fusain, pyrites, and sand in moderate amounts, tended to increase the strength of the cokes obtained above that made from the clean coal. The results, however, varied considerably with the diluting agent used in the agglutinating-power or coking-power tests, and were not entirely conclusive. Accordingly, for the present investigation, a test method was devised which dispensed entirely with the use of a diluent other than the inert material whose effect it was desired to test.

In industrial by-product oven practice, stability of the coke in handling is usually determined by the standard tumbler test of the American Society for Testing Materials (1), or some modification of it. For the work now to be described, the coals and mixtures of coals with various inert materials were coked at coke-oven temperatures in 4-pound charges, and the cokes were tested for comparative size stability and hardness by the tumbler method.

The results of the work are in accord with the previous ones where the agglutinating-power test was used. That is, the addition of fine inert materials commonly contributing to coal ash up to 10 per cent of the charge tends to increase the hardness¹ of the coke as measured by the tumbler test. Pyrites is an exception. It cannot be said that the addition of inert in any case increased the size stability¹ of the coke appreciably. On the other hand, a deleterious effect was not pronounced when inerts in amounts up to 10 per cent were present, except in the case of coarse washery refuse.

APPARATUS

The main requirement in carbonizing apparatus for this work was that it yield cokes of uniform structure so that

¹ The hardness and stability factors of coke are defined by the tumbler test procedure as standardized by the American Society for Testing Materials (1). The stability factor is the cumulative per cent coke remaining on a 1.050-inch (nominal value, 1-inch) square-mesh sieve after treatment in the tumbler machine. The hardness factor is the cumulative per cent remaining on a 0.263-inch (nominal value, 0.25-inch) sieve. Although it is not so stated in the test procedure, stability may be taken as an approximate measure of the tendency of a coke to cross fracture and the hardness factor as an approximate measure of abrasability.

A modified tumbler-test method for the preparation of small samples of coke and for testing their quality is described. When compared with the standard Bureau of Mines 85-pound scale test method, it gave results closely approximating those by the larger scale as regards yield and quality of coke. The method was applied in testing the effect of inerts (washery refuse, gypsum, calcite, pyrites, fusain, and moisture) on the quality of coke made from a Pittsburgh bed coal, with the following results:

- 1. Mineral inerts tend to increase hardness.*
- 2. Except with gypsum, they lower the stability factor, but not excessively, until as much as 1 part inert to 10 parts coal is added.*
- 3. Washery refuse behaves similarly to other inerts when fine but when coarse it greatly decreases stability.*
- 4. Excessive moisture (25.5 per cent) does not seriously affect pore size, but weakens the coke because of the formation of cross-fracture lines.*

reproducible results could be obtained in testing their quality. Another requirement was that the scale of test be as small as practical so that the expense of making the large number of tests required would not be prohibitive. Accordingly, the minimum charge that could be used with this coal was determined by trial. It was found to be approximately 4 pounds (1.8 kg.) with the cylindrical type of retort used, the dimensions of which were 5 inches (12.7 cm.) in diameter by 8 inches (20.32 cm.) high. When a retort of smaller diameter was used, the coke obtained was not uniform, there being excessive amounts of soft, dark coke with large pores at the center of the charge. If a charge of less depth was used, it was difficult to secure sufficient packing of the coal.

The carbonizing apparatus adopted was a small replica of the outfit described by Fieldner, Davis, et al. (3), and used by the Bureau of Mines for the determination of gas and of coke-making properties of American coals. Figures 1, 2, and 3 show the furnace, retort, and complete set-up, respectively. The furnace consisted of a molded fire-clay tube 7 inches (17.78 cm.) internal diameter by 16 inches (40.64 cm.) high mounted on insulating brick, as shown, and provided with a 16-inch (40.64-cm.) steel casing, with heads of transite, containing Sil-O-Cel insulation. The heating element, which was made of No. 3 nickel-chromium wire, was wound in spiral form on a steel mandrel and then placed in the clay tube, where it was protected from contact with the steel retort by a coating of alundum cement. The retort was made from an 8-inch (20.32-cm.) length of standard 5-inch (12.7-cm.) black iron pipe closed top and bottom with sheet steel disks by welding. A 1-inch (2.54-cm.) nipple, welded through the top as shown, served as an outlet for the distillation products. The set-up, Figure 3, shows the retort in place in the furnace, including a glass reflux condenser and Cottrell precipitator² for recovery of the liquor and tar. The gas was measured by a wet test meter of a capacity of 80 feet per hour. Current for heating was supplied by a 7.5-kilowatt regulating trans-

² The writers have been asked repeatedly for details of a simple satisfactory precipitator of this type. The construction will be clear from the figure. Two important points, however, are to be kept in mind: (1) The inner wire electrode must be accurately centered in the bore of the tube. (2) Where a glass tube is interposed between the electrodes, as in this case, a higher voltage than with an iron tube is required. This precipitator tube was supplied by an induction coil capable of giving a 6-cm. spark between needle-point electrodes in the secondary circuit.

former at from 2 to 50 volts in 31 steps, depending on the heating rate desired. A Brown thermoelectric temperature controller, not shown, keeps the temperature constant at the point desired. The tumbler for testing the cokes made in the above apparatus is shown in Figure 4, from which its construction will be sufficiently clear. The drum was mounted horizontally on the shaft of a standard laboratory reducing gear and driven at 22 r. p. m. by a $\frac{1}{8}$ -h.p. electric motor.

PROCEDURE

For making a test, the retort is filled with coal through the off-take pipe with gentle jolting so that the top level of the coal is 0.75 inch (1.9 cm.) from the top. Some coals swell more than others while the charge is plastic, and coals might be encountered where more free space above the charge would be required to prevent stoppage of the off-take. However, the allowance is ample for Pittsburgh gas coal, which has considerable tendency to swell. The furnace is first heated to a temperature of 950°C., and then the retort charged with 1750

For the two largest sizes, square holes cut in $\frac{1}{16}$ -inch (0.15-cm.) steel plate are used, and all the large pieces of coke are tested by hand to find if they will pass the holes in any position. The 0.5-inch (1.27-cm.) and 4-mesh sizes are separated on square mesh sieves.

The cumulative per cent on 1 inch (2.54 cm.) is taken as indicating the relative stability, and the cumulative per cent on 4 mesh is taken as indicating the hardness of the coke.

The gas obtained is calculated to cubic feet of gas saturated with water vapor at 60° F. and 30 inches of water vapor, per ton of charge. The tar recovered in the precipitator is added to that in the distillation-flask receiver and weighed therein together with the distillation water. The water is distilled off and separated from the light oil which comes over with it. This light oil is now returned to the flask, which is again weighed. Both tar and liquor are reported in per cent by weight of the charge.

COMPARISON OF RESULTS, 85-POUND AND 4-POUND SCALE OF TEST

The yield of by-products and the quality of the coke obtained by this apparatus were compared with those from the 85-pound standard carbonizing apparatus (3), which in turn had been standardized against coke ovens and other types of industrial carbonizing equipment. For the purpose of this investigation, it was not essential that the yield of by-products agree precisely with those obtained in industrial practice, but it was required that they be of the same order, since otherwise their quality would be quite different from and not comparable with that of industrial carbonization products. The quality of the coke is, of course, the main point of interest in this work.

Table I shows to what extent the yields of coke, tar, gas, and liquor are reproducible in the 4-pound retort, and Table II shows how the average of these results agrees with results for the same coals obtained in the standard 85-pound retort. Reproducibility of yields in the 4-pound retort is clearly close enough for the present purpose and agreement with results obtained on the 85-pound scale is fairly good. The tar for the 4-pound charge is slightly low, but it is known that the tar yield from the 85-pound retort at 900° C. carbonizing temperature is slightly high as compared with coke-oven practice. The differences in gas yield are somewhat larger than would be desirable in an assay test, and reproducibility of gas yields in the case of coal 1 is hardly as good as would be desirable. No doubt the method could be considerably improved in this regard by further comparative work. At least this has been the experience with the standard 85-pound scale test method.

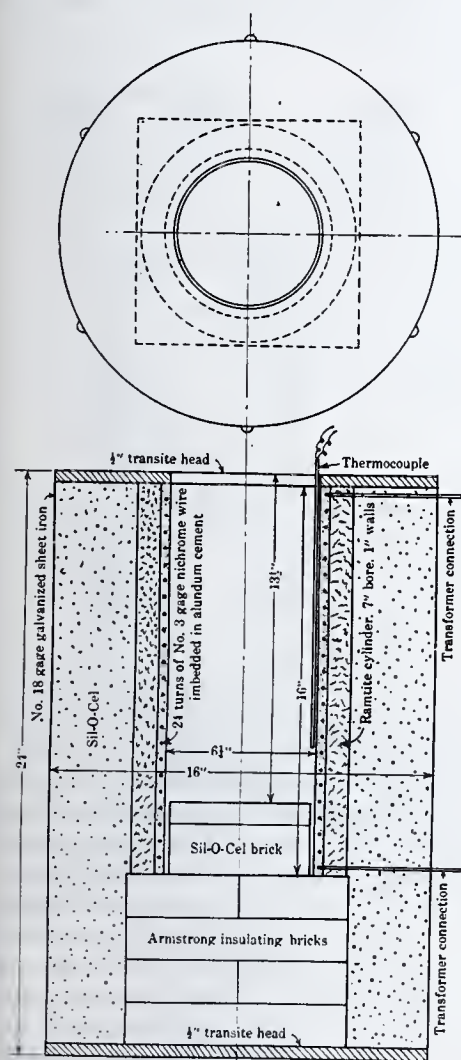


FIGURE 1. FURNACE FOR PRODUCING SMALL QUANTITIES OF COKE

grams of coal, crushed to pass 0.25 inch (0.63 cm.), is lowered into place and quickly connected with the tar recovery train. Charging the furnace with the cold retort causes the temperature of the former to drop quickly to 900° C., at which point the controller is now set. The controller keeps the temperature constant at 900° during the run. As soon as the meter registers 0.3 cubic foot, the precipitator current is turned on and the gas leaving the meter is passed through a large Bunsen burner and burned. The test is continued till the gas flow drops below 0.03 cubic foot per minute, the total time required being approximately 1.75 hours. At the end of the test the retort is removed from the furnace, capped, and allowed to cool, after which it is opened by sawing off the bottom. The coke is then removed, weighed, and sized for testing on the tumbler for which a 1-kilogram charge is used. This charge, which will all pass a 2-inch (5.08-cm.) square opening and remain on one 1.5-inch (3.81-cm.) square, is now placed in the tumbler and rotated at 22 r. p. m. for 1.5 hours, after which it is subjected to the following size analysis:

Through 1.5 inch, on 1 inch.....	%
Through 1 inch, on 0.5 inch.....	—
Through 0.5 inch, on 4 mesh.....	—
Through 4 mesh.....	—

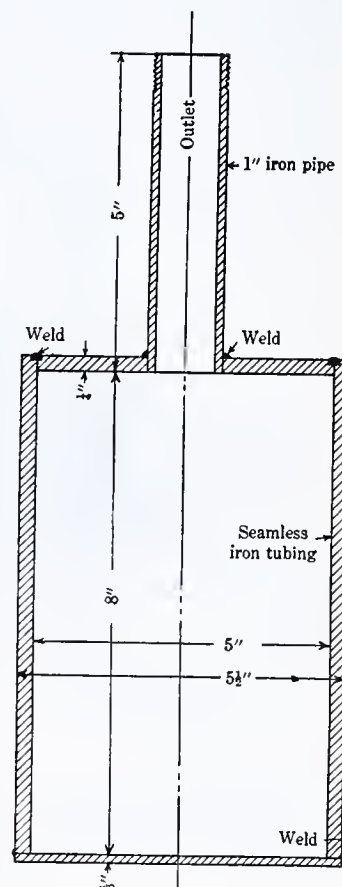


FIGURE 2. RETORT FOR MAKING SMALL QUANTITIES OF COKE

TABLE I. YIELDS OBTAINED WITH QUANTITIES OF 4 POUNDS

COAL	TEST	COKE %	TAR %	LIQUOR %	GAS Cu. ft./ton
1	1	68.3	6.6	4.7	10,010
	2	67.4	6.7	5.1	10,080
	3	68.2	6.8	4.9	10,280
	4	67.9	6.9	4.6	10,120
	5	68.2	7.1	4.9	10,310
	6	68.4	7.0	4.8	10,210
	7	67.6	7.0	5.0	10,190
		Av. 68.0	6.9	4.9	10,170
2	1	64.5	7.7	6.5	10,430
	2	64.3	7.6	6.4	10,470
	3	63.5	7.5	6.6	10,455
	4	64.1	7.6	6.5	10,400
		Av. 64.1	7.6	6.5	10,440

TABLE II. COMPARATIVE YIELDS BY CARBONIZING 85- AND 4-POUND CHARGES OF COAL

	COAL 1		COAL 2	
	85-pound charge	4-pound charge	85-pound charge	4-pound charge
Coke, %	69.2	68.6	64.3	64.1
Tar, %	7.4	6.9	8.0	7.6
Liquor, %	4.7	4.9	6.3	6.5
Gas, cu. ft./ton	10,389	10,170	10,022	10,440

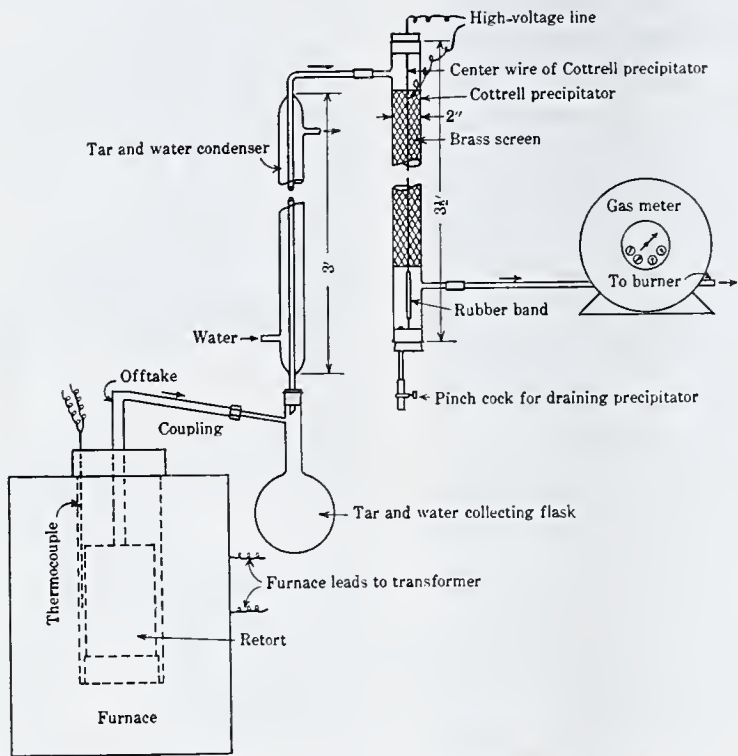


FIGURE 3. SCHEMATIC DIAGRAM SHOWING APPARATUS CONNECTIONS

The behavior of cokes from the 4-pound and 85-pound charges in the small-scale and in the A. S. T. M. standard tumbler tests, respectively, are compared in Table III. It will be noted that the small-scale tumbler test shows a greater difference in the stability factors for the two coals than the A. S. T. M. test, and a somewhat higher hardness factor. Doubtless the small-scale test is not capable of giv-

ing as closely reproducible results as the standard one of larger scale; this is usually the case with highly empirical test methods of this sort. In does seem surprising that the two tumbler-test methods give figures for hardness and stability of so nearly the same magnitude. The following triplicate hardness and stability results for two different coals and for three separate charges in each case indicate the order of reproducibility of the method for testing the quality of coke:

TEST	COKE FROM COAL 1		COKE FROM COAL 2	
	Stability	Hardness	Stability	Hardness
1	58.0	71.0	45.6	74.2
2	55.6	71.3	45.8	74.3
3	57.2	72.1	45.7	73.5
	Av. 56.9	71.4	45.7	74.1

TABLE III. TUMBLER TEST DATA OBTAINED FOR COKES

	COAL 1	COAL 2
MADE FROM 4-LB. CHARGES		
	%	%
On 1.5 inch	13.4	5.5
On 1.5 inch to 1 inch	43.9	40.1
On 1 inch to 0.5 inch	14.1	23.8
On 0.5 inch to 4 mesh	2.0	3.8
On 4 mesh	26.6	25.8
Stability factor	57.3	45.6
Hardness factor	73.4	73.3
MADE FROM 85-LB. CHARGES, A. S. T. M. METHOD		
On 2 inch	0.0	1.0
On 2 inch to 1.5 inch	23.2	20.0
On 1.5 inch to 1 inch	36.1	35.3
On 1 inch to 0.5 inch	10.1	12.3
On 0.5 to 0.25 inch	2.7	3.5
Through 0.25 inch	27.5	27.9
Stability factor	59.3	56.3
Hardness factor	72.5	72.1

ANALYSES OF COALS TESTED

Table IV gives the analyses of the coals used. They are all washery products of the Ocean mine of the Pittsburgh bed in Allegheny County, Pa. The main difference between these coals lies in the sizing. Coal 1 is sized between 3/8 inch (0.96 cm.) and 48 mesh; coal 2 is made up of the same cut but with a large proportion of the coal passing 48 mesh; and coal 3 is a Dorr underflow concentrate all finer than 48 mesh. The last coal contained 25.5 per cent moisture when received, as shown by analysis. The washery refuse was mostly bone and slate, all passing 3/8 inch (0.96 cm.). Coal 1 was used as the clean coal for mixing with the inert materials, washery refuse, gypsum, pyrites, calcite, and fusain in testing their effect on the properties of coke.

RESULTS OF TESTS WITH INERTS

Table V gives results showing the effect on tumbler-test values of adding the inert washery refuse, gypsum, pyrites, calcite, and fusain to coal 1 in the proportions given, before coking. The test of the washery refuse is perhaps the most informative of the series from a practical viewpoint, since the refuse contained all the inert ash minerals in approximately the proportion found in the coal as mined. The writers were

TABLE IV. DESCRIPTION AND ANALYSIS OF PITTSBURGH COALS

COAL No.	DESCRIPTION	LABORATORY No.	BASIS ^a	PROXIMATE ANALYSIS			ULTIMATE ANALYSIS						CALORIFIC VALUE B. t. u./lb.
				Mois- ture %	Volatile matter %	Fixed carbon %	Ash %	Hydro- gen %	Car- bon %	Nitro- gen %	Oxy- gen %	Sul- fur %	
1	Partially cleaned coal from Cham- pion No. 4 washery	A66879	A	0.8	34.5	77.3	7.4	5.1	77.7	1.5	7.2	1.1	13,930
			B	..	34.8	57.7	7.5	5.1	78.2	1.5	6.6	1.1	14,040
			C	..	37.6	62.4	..	5.5	84.6	1.7	7.0	1.2	15,170
2	Clean coal containing large propor- tion of clean -48-mesh coal from Champion No. 1 washery	A66881	A	2.2	36.7	54.0	7.1	5.2	75.0	1.4	8.7	2.6	13,520
			B	..	37.5	55.2	7.3	5.1	76.7	1.4	6.9	2.6	13,830
			C	..	40.5	59.5	..	5.5	82.7	1.5	7.5	2.8	14,910
3	Clean Dorr underflow concentrate made by froth flotation	A70792	A	25.5	22.4	47.2	4.9	10,840
			B	..	30.1	63.5	6.4	14,240
			C	..	32.2	67.8	15,210
4	Washery refuse from Champion No. 4 washery	A77705	A	1.0	15.4	14.3	69.3	1.0	3,520
			B	..	15.6	14.4	70.0	1.1	3,560

^a A, sample as received; B, moisture-free; C, moisture- and ash-free.

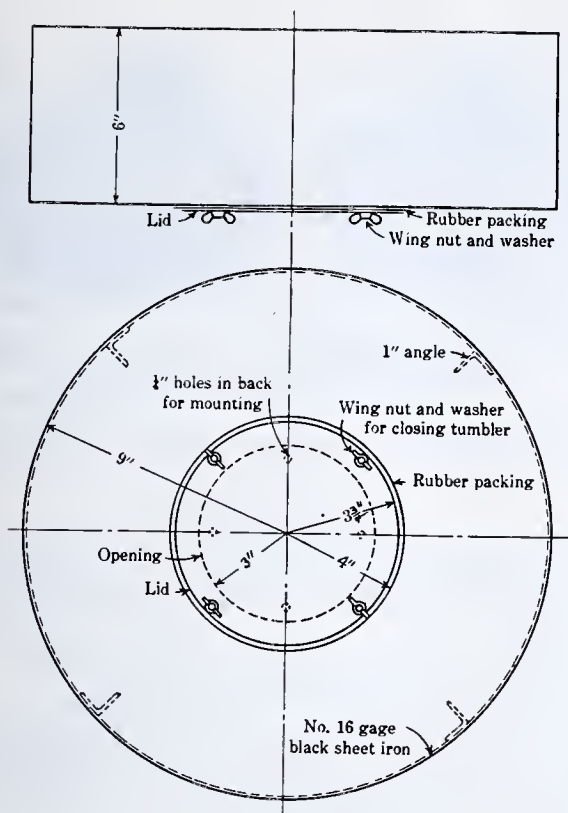


FIGURE 4. TUMBLER FOR TESTING 1-KG. COKE CHARGE

informed by a coke-oven operator using coal from this bed that the coarser sizes of ash-forming minerals affected the tumbler results to a much greater extent than the fine sizes. The comparative test results on $-3/8$ inch and -50 mesh washery refuse bear out this contention, although the effect of the coarse material is not pronounced until a ratio of 10 parts of coal to 1 of inert (approximately 9 per cent of the latter) is reached.

TABLE V. TUMBLER TEST DATA SHOWING EFFECTS OF INERTS

RATIO OF COAL TO INERT	ON 1.5 INCH	1.5 TO 1 INCH	1 TO 0.5 INCH	0.5 INCH TO 4 MESH	THROUGH 4 MESH	STABILITY FACTOR	HARDNESS FACTOR
Pure coal	13.4	43.9	14.1	2.0	26.6	57.3	73.4
Washery refuse, $-3/8$ inch							
100 to 1	6.9	49.9	19.1	1.2	22.9	56.8	77.1
40 to 1	9.5	44.5	20.2	2.2	23.2	54.0	76.8
20 to 1	5.3	49.8	16.5	2.9	25.5	55.1	74.5
15 to 1	6.5	44.7	18.3	2.0	28.5	51.2	71.5
10 to 1	..	33.5	27.0	8.8	31.3	33.5	69.7
Washery refuse, -50 mesh							
100 to 1	11.9	45.1	18.2	1.6	23.2	57.0	76.8
40 to 1	8.3	47.9	16.7	3.5	23.6	56.2	76.4
20 to 1	5.4	49.4	19.5	1.5	24.3	54.8	75.7
15 to 1	7.1	48.3	18.1	1.1	25.4	55.4	74.6
10 to 1	6.0	48.2	16.9	2.0	26.9	54.2	73.1
Gypsum, -50 mesh							
100 to 1	8.5	47.9	19.8	1.1	22.7	56.4	77.3
40 to 1	12.2	43.2	20.3	1.3	23.0	55.4	77.0
20 to 1	14.5	42.4	17.2	2.4	23.5	56.9	76.5
15 to 1	9.4	48.4	16.3	1.0	24.9	57.8	75.1
10 to 1	13.5	44.7	15.2	1.3	25.3	58.2	74.7
Pyrites, -50 mesh							
100 to 1	10.7	43.7	18.4	1.0	26.2	54.4	73.8
20 to 1	7.2	46.5	16.8	2.2	27.3	53.7	72.7
10 to 1	13.0	41.4	13.5	2.2	29.9	52.2	70.1
6 to 1	3.2	49.5	11.5	1.7	34.1	52.7	65.9
Calcite, -50 mesh							
100 to 1	12.5	43.6	17.5	1.6	24.8	56.1	75.2
20 to 1	8.4	44.5	21.3	2.3	23.5	52.9	76.5
10 to 1	9.0	43.5	22.6	2.7	22.2	52.5	77.8
Fusain, -50 mesh							
10 to 1	12.8	42.8	14.1	1.7	28.6	55.6	71.4
6 to 1	13.9	38.5	12.3	3.2	32.1	52.4	67.9
4 to 1	3.0	21.5	19.0	4.9	51.6	24.5	48.4

Strangely enough the tendency of all the inerts is to produce harder cokes than the pure coal, as measured by the modified

tumbler test. It will be recalled that Davis and Pohle (2) found that addition of these same inerts to coal from the same bed increased the resistance of the coke to crushing, as measured by the agglutinating-power test.

Only in one case (that with gypsum as inert) does the stability of the coke as measured by this method show a definite tendency to increase over this testing range. The comparative effect of the various inerts at the 10 to 1 testing ratio arranged in the order of decreasing stability is as follows:

Gypsum.....	58.2
Clean coal.....	57.3
Fusain.....	55.6
Washery refuse.....	54.2
Calcite.....	52.5
Pyrites.....	52.2
Washery refuse ($-3/8$ inch).....	33.5

All these cokes were dry-quenched—that is, the hot retorts containing them were capped and allowed to cool in air, or the capped retort was cooled with water which did not have access to the coke. Cokes made from 10 to 1 mixtures, however, were allowed to stand in the atmosphere of the laboratory to find if such exposure would affect the stability. The effect was noticeable only in the case of the calcite. Lumps of coke containing this inert crumbled, as shown in Figure 5, after 10 days' exposure. Deterioration in this case was very probably caused by slaking of the lime formed from the calcite, and the observation is no doubt of practical importance. Wet-



FIGURE 5. COKE PRODUCED BY 10 TO 1 RATIO OF PITTSBURGH COAL TO -50 -MESH CALCITE, AFTER STANDING 10 DAYS

quenching as ordinarily practiced at coke works would certainly slake the lime present, and even if dry-quenching were adopted, the lime would gradually slake in storage and the coke would deteriorate. It appears important, therefore, that manufactured cokes be low in lime.

TABLE VI. AVERAGE RESULTS OF CARBONIZING -48 -MESH CLEAN PITTSBURGH COAL

	CARBONIZED AS RECEIVED	CARBONIZED AFTER DRYING
Tar, %	4.28	5.69
Liquor, %	28.17	3.42
Coke, %	33.40	69.90
Gas, cu. ft./ton	7310	10010

TUMBLER-TEST RESULTS		
On 1.5 inch, %	Coke of	0.0
On 1.5 inch to 1 inch, %	too poor	49.4
On 1 inch to 0.5 inch, %	quality	22.0
On 0.5 inch to 4 mesh, %	to test	0.7
Through 4 mesh, %		27.9
Stability factor		49.4
Hardness factor		72.1

Excess moisture may be looked upon as an inert, since it contributes no valuable carbonization product and absorbs heat in vaporization. Hofmeister (4) has shown that moisture greatly affects the pressure of a charge of coal during coking. Therefore, it must have some effect on the quality of the coke. Results of tests on coal 3 (Table IV) indicate that this is so. This fine coal was first tested in the "as re-



FIGURE 6. COKE PARTICLES PRODUCED BY CARBONIZING -48-MESH PITTSBURGH COAL CONTAINING 25 PER CENT MOISTURE

ceived" condition (25.5 per cent of moisture) as it came from the concentrator, because it was desired to know its carbonizing properties without further treatment. It was then dried at 110° C. without admitting air to a moisture content of approximately 1 per cent, and was tested again. Table VI gives the comparative results of the tests, and Figures 6 and 7 show the appearance of the cokes. The pore size of the coke made from the wet coal is not more variable than of that from the dried coal. However, the former was excessively ringed with cracks normal to the direction of heat penetration so that it easily fell apart in small pieces not of sufficient size to test. Coke made from the dried coal was somewhat inferior to that made from coarse coal 1 and the mixture of

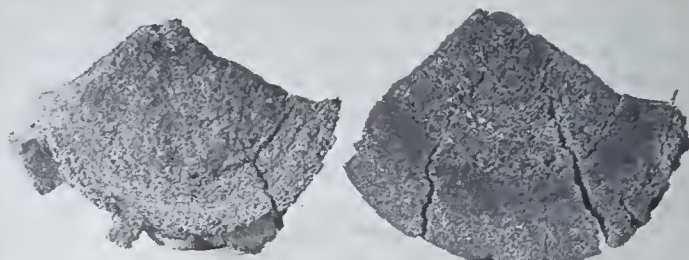


FIGURE 7. COKE PRODUCED BY CARBONIZING -48-MESH PITTSBURGH COAL AFTER DRYING

coarse and fine coal 2, as reference to results in Table III will show.

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- (3) Fieldner, A. C., Davis, J. D., Thiessen, R., Kester, E. B., and Selvig, W. A., *Bur. Mines, Bull.* 344 (1931).
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Solving Higher Degree Equilibrium Equations with Polyphase Duplex Slide Rule

MILTON J. POLISSAR, University of California, Berkeley, Calif.

A FEW months ago the writer had occasion to solve a fifth-degree equilibrium equation of a type that could not be readily solved by the method of successive approximations. He then devised a procedure whereby the unknown was found in a very short time and without much effort. Since then, this procedure has been used in the solution of many other equations, and its use has been accompanied by a saving in time and in mental effort.

The principle involved is simple, and it is probable that a large number of individuals are using it, but the writer has not found this method mentioned in any of the several slide rule manuals examined recently.

Many equilibrium equations can be reduced to the form:

$$(x + a)^m \cdot (x + b)^n = K \quad (1)$$

in which m and n are small integers, positive or negative. In applying the present method, the first step consists of replacing Equation 1 by a set of two equations containing monomials instead of binomials:

$$U^m \cdot V^n = K \quad (2)$$

$$U - V = a - b \quad (3)$$

$$(x = U - a = V - b) \quad (4)$$

In certain cases it is possible to set the slide of a slide rule in such a way as to obtain all the pairs of solution of Equation 2. It remains only to pick out that pair which will also satisfy Equation 3, and the problem is solved. In other cases it is necessary to manipulate Equation 2 and possibly invert or reverse the slide before a setting is obtained from which the pairs of solutions can be obtained by reading the proper scales.

APPLICATION OF METHOD

Let us now consider a few equations and apply the procedure outlined above for their solution.

$$\text{I. } (x + 7) \cdot (x + 3) = 35$$

This equation can be developed into a quadratic and solved by means of the standard formula. However, even in this case the solution can be obtained much more rapidly by finding two numbers, U and V , such that their product is equal to 35 and their difference is equal to 4. Figure 1 shows the slide setting that gives directly all the pairs of numbers whose product is equal to 35. U is read on the D scale, and V is read on the (reciprocal) CI scale. By sliding the hairline along the rule, we find, after testing a small number of pairs, that 8.25 and 4.25 are the two numbers whose product is 35 and whose difference is 4.00. Hence, x is equal to 1.25.

$$\text{II. } (x + a)^3 / (x + b) = K$$

As an illustration we shall find the degree of hydrolysis of a 0.08-formal solution of chlorine at 25° C. The equilibrium constant is $K = 4.84 \cdot 10^{-4}$.

Let the degree of hydrolysis be equal to x . The following equilibrium equation must be satisfied:

$$\frac{x^3 c^2}{(1 - x)} = K \quad (5)$$

where c is the formality of the chlorine. For very small values of c , the value of x is given quite accurately by the formula:

$$1 - x = c^2 / K$$

For intermediate concentrations, the value of $1 - x$ can be obtained by the method of successive approximations, using the formula:

$$1 - x = x^3 c^2 / K$$

and starting with the assumption that the hydrolysis is practically complete, and that x^3 is practically equal to unity. For a 0.08-formal solution of chlorine such an assumption would lead to an impossible value of x . One could start with the assumption of a reasonable value of x and arrive at the correct one by the method of successive approximations, but the following procedure is speedier and more direct.

By a transformation of Equation 5 we get:

$$\frac{1 - x}{x^3} = \frac{c^2}{K} = \frac{64 \times 10^{-4}}{4.84 \times 10^{-4}} = 13.23$$

$$\frac{(1 - x)^{1/3}}{x} = 2.361 \quad (6)$$

Replace Equation 6 by the following pair:

$$\frac{U^{1/3}}{V} = 2.361 \quad (7)$$

$$U + V = 1.00 \quad (8)$$

Invert the slide (by rotating it 180 degrees around its longitudinal axis). Set 1 on the C scale against 2.361 on the D scale (Figure 2). This setting gives all the pairs of numbers, U (to be read on the K scale) and V (to be read on the C scale), which satisfy Equation 7. Moving the hairline along the rule we find that the pair of numbers $U = 0.636$, $V = 0.364$ also satisfy Equation 8. Hence, $x = V = 0.364$, and we find that the hydrolysis is 36.4 per cent complete.

$$\text{III. } \frac{(x + a)^3}{(x + b)^2} = K$$

This equation can be transformed as follows:

$$\frac{(x + b)^{2/3}}{(x + a)} = C \quad (9)$$

$$\frac{U^{2/3}}{V} = C \quad (10)$$

$$U - V = b - a \quad (11)$$

$$(x = U - b = V - a)$$

Set 1 on the B scale against C on the A scale. The two scales are now coupled in such a way as to give all the pairs of numbers whose ratio is equal to C . Figure 3 is self-explanatory and shows that U should be read on the K scale, and V on the B scale. It remains to select the pair whose difference is equal to $b - a$.

$$\text{IV. } (x + a)^3(x + b)^2 = K$$

Transforming this equation, we get:

$$(x + b)^{2/3}(x + a) = C$$

$$U^{2/3}V = C$$

Reverse the slide (by rotating it 180 degrees in its own plane). Set 1 on the B scale against C on the A scale. Note that B now functions as a reciprocal scale. It is coupled with the A scale in such a way that the *product* of the pairs of numbers is equal to C . It will be seen from Figure 4 that U and V should be taken from the K and the B scales, respectively. Again, that pair should be selected whose difference is $b - a$.

CONCLUSIONS

It should be pointed out that this is essentially a trial and error method; that its chief merit lies in the ease with which the guesses can be tested; and that its usefulness is the greater, the smaller the number of guesses before the correct one is made. Just as one can waste a great deal of time weighing a sample if one does not proceed systematically, so one can spend a great deal of time arriving at the correct solution, unless a systematic procedure is used. The following arrangement was tried and found satisfactory.

The values of U and V are recorded in two parallel horizontal rows. Their sum (or difference, as the case may require) is obtained directly and recorded in the third row. The first guess usually gives a decidedly low or high value for the third quantity. It will be found generally that the

Fig. 1. Solutions of the equation: $U \times V = 35$

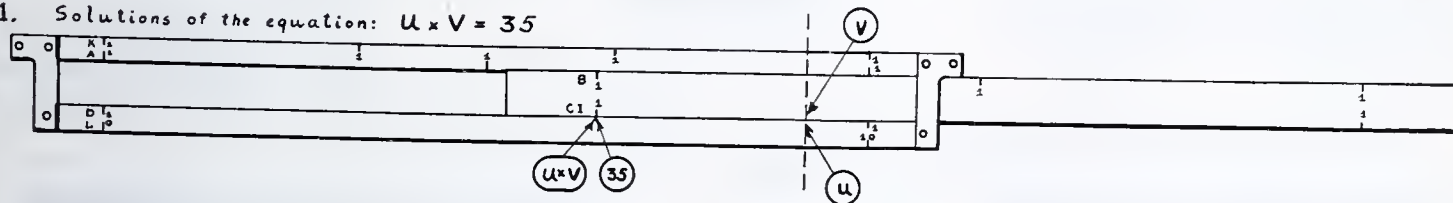


Fig. 2. Solutions of the equation: $U^{1/3} : V = 2.361$

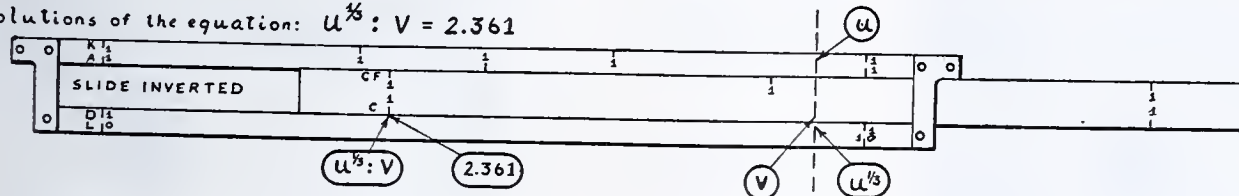


Fig. 3. Solutions of the equation: $U^{2/3} : V = C$

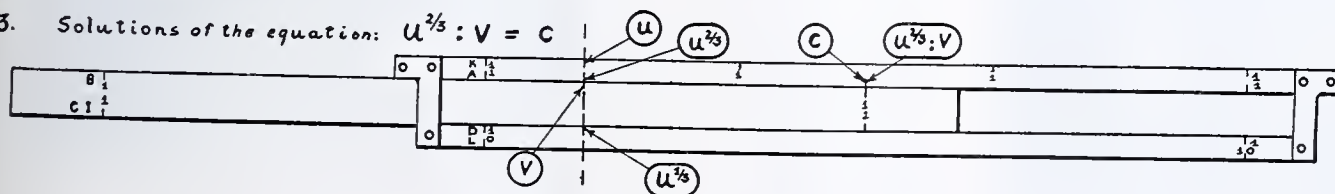
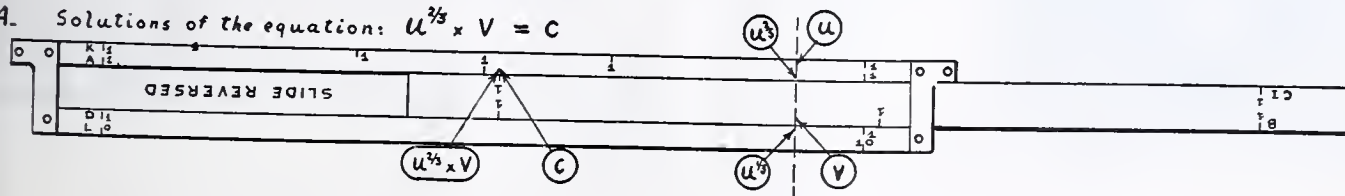


Fig. 4. Solutions of the equation: $U^{2/3} \times V = C$



scales from which the first two quantities were taken have different number densities. The scale with the larger number density will determine the direction in which the hairline should be moved to give the desired sum (or difference). After this

it takes three or four more guesses, and the solution is obtained with slide rule accuracy.

RECEIVED March 28, 1932.

Improved Unit for Removal of Solid Particles from Gas Streams

R. C. STRATTON, J. B. FICKLEN, AND EDW. W. KRANS

Travelers Insurance Company and Travelers Indemnity Company, Hartford, Conn.

IN A recent study of metallic fumes and particles in air, it was necessary to use an apparatus for the absorption of the particles in a suitable dissolving acid when the rate of flow of the air varied between 0.2 and 1.0 liter per minute.

Several types of gas-washing units were tried, such as the ordinary type of gas-washing bottle, a bottle having a glass spiral, a porous, fritted plate bubbler, and a bottle provided with an impinger unit so arranged that the gas or air stream struck the bottom of the bottle at a relatively high velocity. None of these absorption units proved entirely satisfactory. After considerable experimentation the apparatus shown in Figures 1, 2, and 3 was developed and gave surprisingly efficient and uniform results.

The material necessary for the construction of one absorption unit is as follows:

- 1 piece Pyrex glass tubing, 9 mm. outside diameter
- 1 Pyrex hydrometer jar, 52 × 200 mm. inside dimension
- 1 Coors porcelain Gooch crucible No. 4, glazed
- 1 No. 7 rubber or cork stopper
- 1 No. 11 rubber or cork stopper

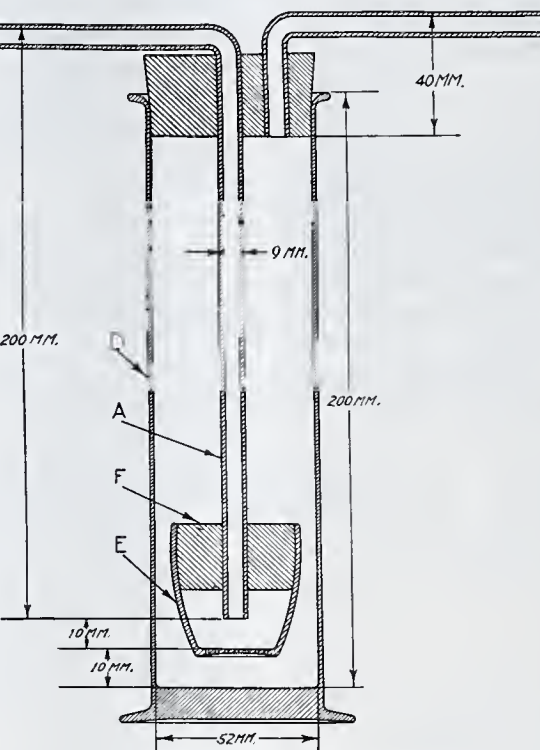


FIGURE 1. DIAGRAM OF APPARATUS

Referring to Figure 1, tube A should be inserted in stopper F so that the end of the tube is 10 mm. from the bottom of Gooch crucible E and the crucible placed so that the bottom of the crucible is 10 mm. from the bottom of the bottle. The assembly A should be so located as to be in the center of jar D.

Figures 2 and 3 show the unit which was used in this laboratory.

The air to be sampled is drawn through tube A against the bottom of crucible E, where the air or gas stream is broken up and allowed to pass through the holes of the crucible into the washing solution in a series of small bubbles, after striking against the bottom of bottle. As the bubbles rise through the solution their progress is somewhat retarded between the sides of the Gooch crucible and the jar, thereby giving a slight scrubbing action. The effects just mentioned tend to give surprisingly good quantitative results in the removal of foreign materials from the gas stream.

It was found that 150 ccm. of washing solution were satisfactory for general purposes when using this apparatus.

The use of this unit is not confined to sampling air for metallic dust particles, but may be used for sam-

pling air for dust counting, the absorption of vapors, gases, and many other applications.

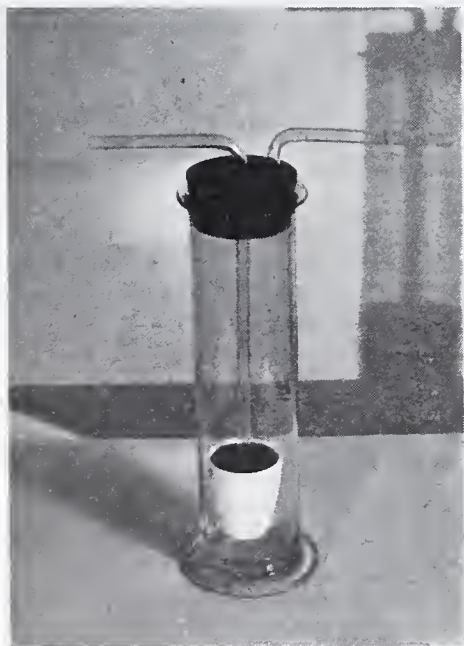


FIGURE 2. SET-UP OF APPARATUS

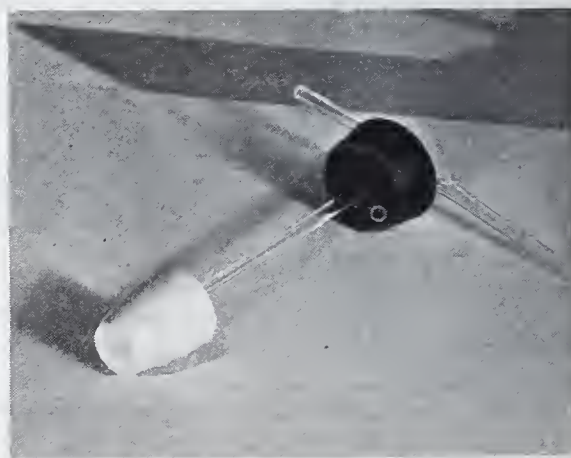


FIGURE 3. CRUCIBLE WITH TUBES IN PLACE

This unit should find favor with investigators because of its simplicity of construction, its low cost, and its high degree of efficiency.

RECEIVED February 29, 1932.

Simple Evaporation Tests for Mineral Oils

J. J. SHANK, The Wayne Laboratories, Waynesboro, Pa.

DURING the course of some work undertaken at this laboratory for the purpose of assisting clients to obtain information relative to various desirable properties of petroleum oils for use in a manufacturing process, the necessity of making comparative determinations of the volatility of different oil samples became apparent.

It has been found useful to impregnate certain varieties of crushed rock granules with oil when these granules are to be used as a surfacing on asphalt felt roofing. This treatment is given in order to eliminate to some extent certain conditions which arise when the surfacing is applied to the felt, among which are blistering and staining of the granules.

The volatility tests now in use do not give results which indicate what may be expected when mineral oils are exposed to evaporation (and oxidation) under such conditions. It is felt that under such conditions there is an accelerated evaporation and oxidation which is entirely different from the volatilization observed when conducting a test under A. S. T. M. designation D 6-30 (1). Since the result desired was to be an expression of the rate of volatilization and oxidation for a given sample when spread out upon a relatively large and uneven surface, and it was desired to compare various samples of oil to obtain a sample which was most constant under such conditions, it was felt that a method could be devised which would give this information with more certainty than the procedure outlined under D 6-30.

The following method has been found very satisfactory when used for comparing the changes obtained with various petroleum oils when subjected to the conditions of the test. The procedure is designed to simulate as closely as possible actual exposure conditions on the roof in regards to area and surface exposed. The results obtained agree very closely, and it has been found possible to reproduce them at will.

METHOD

The method requires the use of a shallow porcelain dish having a diameter of 70 mm., a depth of 10 to 12 mm., and a capacity of 45 ml. The porcelain dish supplied by the Arthur H. Thomas Company, Philadelphia, Pa., Catalog No. 4484, Size 1, meets the requirements and was the dish used in these experiments. In addition, there will be required a quantity of ordinary lead shot, Size 6. This lead shot is carefully dried and stored in a desiccator until used.

Place 44 grams of lead shot (\approx 1 shot) in the porcelain dish and weigh the dish and shot accurately. Add from a weighing bottle fitted with a dropping pipet 0.3 gram of the oil to be tested. This should preferably be done while the dish is on the balance pan, since this will eliminate the necessity of weighing the oil and the weighing bottle. This amount of shot and oil has been worked out so that there is a sufficient quantity of shot to present a large oil surface to the oven atmosphere when a 0.3-gram sample is used. Place the dish and its contents in an ordinary electric drying oven which has been brought to a temperature of 60° C. Allow 15 minutes for the dish and contents to attain the temperature of the oven, and then heat the sample for 5 hours maintaining the temperature constant at 60° C. Remove, cool in the desiccator, and weigh rapidly when cold. Calculate the loss in weight as volatile matter at 60° C. under test conditions as outlined.

The lead shot serves to break up the sample of oil and present a large area for a given volume in the form of a film.

No comparison has been made between this method and the standard A. S. T. M. method of test, D 6-30. It is quite possible that there will be little if any agreement. It is felt, however, that the method as outlined is a good indication of the relative volatility of the various petroleum oils which we are called upon to test. This is more particularly true since, under the conditions of use, the oil will be spread over a large surface, thus presenting a large area for evaporation. Comparisons with samples of oil of equivalent weight but tested without the addition of lead shot show that the results are higher when the shot is used. This was expected, since it was felt that the addition of lead shot would in a sense produce an accelerated volatilization. The increase was practically proportional when the results on various samples were compared by both methods. A small amount of additional work seems to indicate that so long as the size of the sample is kept reasonably small there is little or no difference in results, whether they are determined on catch weights or on exactly 0.3-gram samples. The main point seems to be that only enough oil should be taken so that it is evenly distributed over the shot without covering it completely, thus insuring a large surface for evaporation.

RESULTS

The following figures of actual tests performed in duplicate are indicative of the results obtained by this method:

OIL	LOSS WITH SAMPLE 1	LOSS WITH SAMPLE 2
	%	%
1	0.12	0.12
2	0.26	0.20
3	0.22	0.23
4	0.48	0.49
5	0.57	0.60
6	0.22	0.18
7	0.14	0.12
8	0.25	0.25
9	0.14	0.12
10	0.09	0.09
11	0.12	0.09
12	0.06	0.06
13	0.12	0.18
14	0.37	0.41
15	0.27	0.31

NOTE. Catch weights of approximately 0.3 gram were used in these determinations.

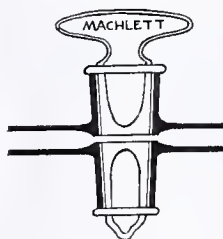
The possibility of oxidation of oil has not been overlooked, but no work has been done on this feature.

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RECEIVED February 29, 1932. Resubmitted May 21, 1932.

New Hollow Glass Stopcock



A hollow stopcock plug, devised by R. R. Machlett, 50 William St., Long Island City, N. Y., is built from a single piece of glass with the bore drilled through it in exactly the same manner as for a solid plug. This procedure gives plugs made by the new method all the advantages of the old hollow plugs with none of their disadvantages—leakage, tendency to freeze, and high cost. All the customary styles of stopcocks—straight, two-way, three-way, oblique, etc.—are available built by the new method.

Rinnmann's Green Test for Zinc

A. A. BENEDETTI-PICHLER, Washington Square College, New York University, New York, N. Y.

THE formation of Rinnmann's green is generally recognized as one of the best methods of confirming the presence of zinc, and the test is recommended by all of the outstanding textbooks on qualitative analysis (2, 7, 8). Up to the present, however, there has been no perfectly satisfactory way of carrying out the test. This can be easily understood from a discussion of the reactions involved.

According to Hedvall (6), the so-called Rinnmann's green consists of mixed crystals of zinc oxide and cobaltous oxide.

The mixed crystals are obtained by heating the oxides to about 800° C. On heating for a long time at 1100° C., the crystals will be obtained as hexagonal plates, needles, and pyramids of about 2 to 3 mm. in length.

Owing to the limited solubility of cobaltous oxide in zinc oxide, it is found, after ignition, that more than 1 part of cobaltous oxide to about 10 parts of zinc oxide produces reddish brown crystals of cobaltous oxide in addition to the green mixed crystals. With a further increase in the amount of cobaltous oxide present, it finally becomes impossible to confirm the presence of green mixed crystals. Furthermore, though the cobaltic oxide, Co_2O_3 , is not stable above 900° C., oxidation of the cobaltous oxide present in the mixed crystals may take place in the temperature range from 900° to about 300° C. when the preparation cools to room temperature. The cobaltic oxide formed then gives a solid solution with the cobaltous oxide, and the color of the preparation changes to brown or black.

Therefore, in order to obtain a good Rinnmann's green test the following requirements must be fulfilled:

1. Zinc and cobalt must be used in the form of oxides or compounds which are easily transformed to oxides on ignition (nitrates, carbonates).

2. Zinc and cobalt must be present in certain proportions. Especially must an excess of cobalt be avoided. An excess of zinc oxide is by far less dangerous because it acts more or less as a colorless solvent. In the presence of not too large an excess of zinc the green color becomes paler but can be perceived.

3. While hot (below 900° C.) the preparation must be protected against oxidation (presence of a reducing agent—e. g., charcoal or filter paper as carrier of the test—or imbedding in an inert slag), or it must be cooled rapidly through the dangerous temperature range.

Accordingly, aside from the special method of carrying out the test, it is usual to avoid an excess of cobalt by adding a very dilute solution of the latter in small portions to an assumed excess of the zinc preparation, and to repeat the test with increased quantities of cobaltous nitrate until a definitely green residue is obtained.

Emich (3) was the first to attempt an automatic adjustment of the zinc-cobalt ratio. He allowed a droplet of the unknown solution and a 1 per cent cobaltous nitrate solution to diffuse toward each other in a narrow strip of filter paper which was then dried and ignited. It was expected that the

Rinnmann's green test for zinc can be carried out in a very simple way by placing a drop of the test solution on a piece of filter paper impregnated previously with potassium cobaltcyanide, drying, and ashing the paper; 0.0006 mg. of zinc still produces a disk of green ash on the spot where the solution had been added. The test is best carried out with a solution obtained by dissolving the zinc sulfide precipitated in the course of a separation in nitric acid. Some of the limit proportions for the presence of other metals are given. The reasons for the reliability of the technic employed may be seen from the discussion of the reactions involved.

correct ratio zinc-cobalt would finally prevail in some zone of the strip, but this method occasionally failed.

Later Emich thought that if a compound containing the cobalt and the zinc in the proper ratio is first prepared, chance could no longer influence the result. He also pointed out that zinc cobaltcyanide, which can easily be obtained by precipitation with potassium cobaltcyanide from an acid solution, seems to possess the desirable properties.

The zinc cobaltcyanide of approximately the formula

$\text{Zn}_3(\text{CoCy}_6)_2$ ¹ resembles the corresponding ferricyanide very closely with respect to crystal form and solubility. It forms a white finely crystalline precipitate which is very difficultly soluble even in acid solutions. On ignition it gives zinc oxide and cobalt oxide in the ratio 3 to 2. Therefore, not all of the cobaltous oxide formed can be dissolved by the zinc oxide. As a result of the ignition we may expect a mixture of mixed crystals and crystals of cobaltous oxide. In fact, the Rinnmann's green obtained in this way exhibits a brownish hue.

It was shown that it is possible to confirm the presence of very small amounts of zinc by precipitating a droplet of the unknown solution on a narrow slide with potassium cobaltcyanide, washing the precipitate with dilute nitric acid, drying, and igniting on the slide. Even with a little less than 10^{-4} mg. of zinc it was possible to identify the Rinnmann's green formed under the microscope by its color and shape (pseudomorphic crystals showing the square-shaped outlines of the former zinc cobaltcyanide crystals, 1). The properties of the zinc cobaltcyanide and of the Rinnmann's green can be investigated in succession even with a single crystal of the former compound.

It is obvious that the reliability and sensitivity of this procedure cannot be surpassed. It has only one disadvantage. In carrying out the ignition on the slide, the slightest overheating causes complete oxidation of the small quantities of Rinnmann's green and, therefore, the ignition must be carried out in a current of inert gas (carbon dioxide). This, of course, renders the procedure complicated and will cause many to refrain from using it.

For the student's use in qualitative analysis the author has always recommended the old practice of soaking a piece of filter paper in a solution containing zinc and cobaltous nitrate, drying, and ashing. Under these conditions failure due to oxidation of the Rinnmann's green already formed never results. This may be due to the protective action of the gaseous products formed by the burning paper, or to the rapid cooling of the small quantity of ash. The ash of the paper may also have an effect. Of course, the test is often spoiled by adding too much of the cobaltous nitrate solution.

The next step was obviously to try the precipitation of the zinc cobaltcyanide in filter paper followed by ashing of the paper. This method, using the automatic adjustment of the

¹ Cy = Cn.

zinc-cobalt ratio and a carrier for the test which prevents oxidation during the ignition, appears to be satisfactory in every respect. It combines reliability with sensitivity and outstanding simplicity.

PROCEDURE

According to the technic involved, the test described may be classified as a spot test (5).

The necessary reagent paper is prepared by soaking "ash-free" filter paper in a solution of 4 grams of potassium cobalticyanide and 1 gram of potassium chlorate in 100 cc. of water and drying at room temperature or at 100° C.² When slightly heated, this paper bursts into flame and leaves a perfectly black ash consisting mainly of cobaltous oxide.

For carrying out the test, two ways may be suggested, depending upon the quantity of zinc available.

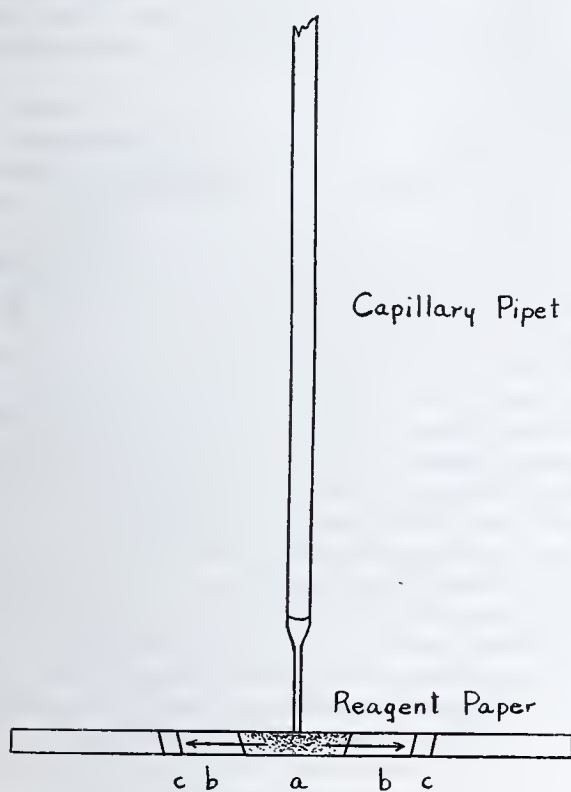


FIGURE 1

MACROTECHNIC. By means of a glass rod transfer one drop of the test solution to the center of a piece of cobalticyanide paper about 1 inch (2 cm.) square, which is held horizontal by means of a forceps. When the drop is completely absorbed, dry by holding the piece of paper high above a small Bunsen flame. A yellow line will appear first along the outline of the drop. Continue drying until the center turns brown. Then light the paper. Place the ash on a clean porcelain dish or plate for inspection. In case zinc is present, a disk of green ash will be visible on the spot where the drop of solution had been added. The green disk is always surrounded by a circular zone containing very little ash. Sometimes it is connected with the surrounding sheet of black ash only by a delicate network of black fibers. This phenomenon is more pronounced when using the second procedure.

MICROTECHNIC. The size of the cobalticyanide paper may be decreased to less than one fourth of the aforementioned. First take the test solution up into a micropipet, a glass capillary of 0.5- to 1-mm. bore with a finely drawn out point of about 0.1-mm. bore at the opening. Touching the center of the reagent paper with the point of the capillary pipet, the solution is sucked into the paper and is spread out in all directions. The arrows in Figure 1 indicate the direction of the flow of the liquid.

It is self evident that the zone around the point where the solution enters the paper, *a*, will finally contain the zinc cobalticyanide precipitate and probably (and favorably) also some zinc nitrate in excess, because toward the end the potassium cobalticyanide originally present will already be used up. Zone *b* finally will

contain only a small amount of salts, the potassium cobalticyanide originally present being rinsed out by the liquid coming from zone *a*. In zone *c* the salt concentration becomes increased. When the paper is dried and ashed as already described, the Rinnmann's green will appear in the center zone, *a*, and zone *b* will form the ring zone containing little ash. The final appearance of the test depends, of course, not only upon the absolute amount of zinc present, but also on the concentration (and volume) of the zinc solution, etc. It is obvious that the study of ash pictures obtained in similar experiments might offer a means for the investigation of diffusion and adsorption phenomena.

Of course, a very small amount of zinc cannot form a disk of green ash. In this case only a small thread or a delicate network of green fibers will be found, but the green color can be distinctly observed under the microscope using a low-power objective and reflected light. Daylight illumination is, of course, most convenient for the inspection of colored objects.

SENSITIVITY OF TEST

The zinc solution used for the test should be acid. The sensitivity of the test was determined using solutions containing about 5 per cent free nitric acid. The following limits (4) were found:

Macrotechnic:

Limit concentration,	1 mg. zinc/cc.
Limit of identification, about	0.05 mg. zinc

Microtechnic:

Limit concentration,	0.4 mg. zinc/cc.
Limit of identification, about	0.0006 mg. zinc
(Droplets of 1 to 4 cu. m. volume used)	

But it must be pointed out that the Rinnmann's green test is to be used only after separation of the zinc from most of the other elements. Tin and antimony can also give a green ash. A drop of 1 per cent titanium solution causes an intense blue color of the ash. More dilute (0.2 per cent) titanium solutions give a gray ash. The presence of larger amounts of other metals, such as manganese, iron, cobalt, nickel, or cadmium, interfere with the test, because they also give precipitates with potassium cobalticyanide and dark residues on ashing. The following limit proportions (4) may be mentioned: Zn : Cd = 1 : 5; Zn : Mn = 10 : 1; Zn : Co = 2 : 1; Zn : Ni = 1 : 1; Zn : Ti = 1 : 1; Zn : Al = 1 : 2 (aluminum gives a light blue ash).

It will be seen that it is especially necessary to remove the manganese completely.

Dark-colored zinc sulfide obtained in the course of a separation is best redissolved after washing. The solution is treated with sodium hydroxide and sodium peroxide in order to remove nickel, cobalt, manganese, and iron. From the filtrate the zinc is again precipitated as sulfide, which is finally dissolved in a small volume of 2 *N* nitric acid, and this solution used for the Rinnmann's green test. It is not necessary to adjust the acidity of the solution very carefully, as the test works also with strongly acid solutions (30 per cent nitric acid).

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RECEIVED December 7, 1931.

² Addition of potassium chlorate is not essential. The "cobalticyanide paper" may also be ordered from Microchemical Service, 30 Van Zandt Ave., Douglaston, N. Y.

A New Type of Electrolytic Cell

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PORCELAIN cells are used extensively as diaphragms in electrochemical processes, both organic and inorganic, and the conventional, round, white cell is a familiar sight to all workers in this field of chemistry. Commercial cells used for some types of electrochemical work are unsatisfactory, however, in that they do not seem sufficiently porous. Further, difficulty is experienced in that the commercial cells, after 36 to 100 hours of service, begin to disintegrate, and pieces of the outer surface of the cell "spall off" into the electrolytic bath.

The purpose of this paper is to describe a new type of electrolytic cell devised for inorganic electrochemistry. The length of service derived from this new type of cell is in striking contrast to the service obtained from the commercial round cell. One of these new cells has been in use for over a year and as yet has shown no serious deterioration. The porosity of the cell is also considerably greater than that of the usual commercial cell.

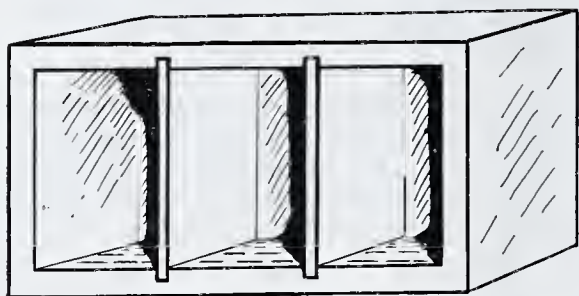


FIGURE 1. DIAGRAM OF MULTIPLE-CELL BOX

Although it is possible to make the ordinary round type of commercial cell by the casting process, the writers found it more convenient to make thin plate-like diaphragms which were used as partition diaphragms between the cells of a multiple electrolytic cell box. The multiple-cell box in which the diaphragms were used was of stoneware, consisting of three cells, made especially for the diaphragms.

THE DIAPHRAGMS

The mixture used in casting the diaphragms, expressed in parts by weight, was as follows:

French flint.....	1 part
Kentucky ball clay.....	2 parts
English china clay.....	2 parts

The three ingredients were first sifted through a 100-mesh screen and then mixed with a sufficient quantity of water to produce a slip of fairly low viscosity. This clay-flint-water mixture is generally known as a "casting slip."

In preparation for the casting of the diaphragms, a shallow tray with sides at least 1.5 inches (3.81 cm.) in height and a plaster of Paris floor 1 inch (2.54 cm.) in thickness was constructed. The tray measured approximately 1 foot (.304 meter) square. The casting slip was poured into this tray until it covered the plaster floor to a depth of about 0.16 inch (0.42 cm.). A slight jarring of the tray during the pouring of the mixture spread the slip uniformly over the floor of the tray.

The plaster floor of the tray absorbed the excess water from the slip rather rapidly, and in less than an hour the casting had "set," although it was still moist and comparatively soft. At this stage the casting was divided into 3-inch

(7.62-cm.) squares with the aid of a spatula. The squares were then allowed to dry thoroughly in air.

THE MULTIPLE-CELL BOX

The stoneware multiple-cell box and the method of fitting the diaphragms into it are shown in Figure 1.

The cell box was approximately 5 by 2.5 by 2.25 inches (12.7 by 6.35 by 5.71 cm.) outside dimensions, and was built by hand from an Indiana underclay (fire clay) having a refractoriness of Cone 10 (standard pyrometric cone scale). The box was glazed with Albany slip glaze. (The Albany slip glaze is a standard product and can be secured from any firm dealing in ceramic supplies.)

In the construction of the stoneware box, a wooden box-mold slightly larger than the desired cell box was used. The underclay, after being ground and screened, was mixed with water to a fairly stiff plasticity, rolled into a sheet approximately 0.25 inch (0.63 cm.) in thickness, and then cut into strips 2.75 inches (6.98 cm.) in width and 5.5 inches (13.97 cm.) in length. One of these strips was placed on the floor and one along each of the inside walls of the wooden mold. The edges of the strips were slightly moistened and, by pressure of the fingers, were easily "welded" together at the corners and along the floor seams. All joints inside the box were further welded and smoothed over with a spatula. The box could now safely be slipped out of the mold, and all exterior joints and seams were welded and smoothed over. The cell box was allowed to air-dry for an hour or two, but while still appreciably moist, two grooves, about 0.16 inch (0.42 cm.) wide and 0.13 inch (0.31 cm.) deep, were cut in each side and across the floor of the box. The grooves form slots for holding the diaphragms in position. After cutting the grooves, the cell box was completely air-dried and then further dried for 8 hours in a desiccator heated to 100° C.

FINISHING CELL BOX

On removal of the cell box from the desiccator, the diaphragms were trimmed to fit the prepared slots in the cell box and were slid into position. Care was exercised to see that the diaphragms fit snugly into the slots. With the diaphragm in place, the entire cell box was dipped into a thin slip of Albany glaze. The glaze was allowed to air-dry before the cell box was again sent to the desiccator where it was given a second drying of 4 hours at 100° C.

On removal from the desiccator this second time, the raw glaze was thoroughly scraped off the diaphragms to within 0.25 inch (0.63 cm.) of their margins. The cell box was fired in a muffle kiln until the glaze "matured."

The type of glaze used on the cell box matures about Cone 4, and experimentation has demonstrated that this temperature is sufficient to produce the desired porosity of the diaphragms as well as burn the body of the cell box to a well-fused condition. The porosity produced at this heat in a diaphragm composed of the mixture used by the writers is considerably higher than the porosity of the commercial cell and has proved satisfactory for the type of research for which the diaphragms have been used.

CONCLUSIONS

The cell-box described above has several points of merit. In the first place, the multiple-cell feature of the box is

desirable as it gives a very compact unit containing two cells for the electrodes and a central supply cell. Further, the stoneware box and its cells are glazed with a material that is resistant to most acids and bases, and therefore is well adapted to chemical work. The diaphragms are sealed into place by the glaze and danger of leakage around them is impossible as long as the glaze remains intact. Sealing of the diaphragms into position by the glaze also allows the use of the cell box for heated and strongly alkaline solutions; this would not be possible if a wax seal were used.

The composition of the mixture used in the diaphragms is similar to that used in the manufacture of commercial cells.

The writers do not claim any originality for that feature, but the casting method of making these diaphragms is felt to be an improvement over the commercial cell made by dry-press methods. Casting of the diaphragms has resulted in a more uniformly porous product free of spalling, and it is believed that this method of making diaphragms has a practical value. It is entirely possible to make the electrolytic cells in the usual round shape by casting methods, and the writers are of the opinion that the present commercial cell can be improved by manufacturing such cells by the casting process instead of by the present dry-press methods.

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Capacity of Drying Agents for Gas Masks

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DRYING agents for the removal of water vapor from gases are generally employed on the basis of their aqueous tension, and as a rule the investigator assumes the use of unlimited amounts depending merely on the drying ability rather than the drying capacity. When specifications limit the space which may be occupied by a drying agent, as is the case in gas-mask canisters, the problem becomes quite different. Here it is necessary not only to know the aqueous tension of the dryer, but also its life, or in other words, its capacity, in the limited space which it occupies. Were one able to depend on theoretical values for the water which can be taken up by anhydrous substances to form definite hydrates, he might be inclined to think that the life of the dryer could be extended to this limit. Where data are available on the aqueous tension of hydrates, the amount of moisture which can escape is known. Certain substances such as calcium chloride and phosphorus pentoxide will, as we know, continue to absorb water beyond the point where definite hydrates have formed. Here we are not only confronted with a tendency toward increasing aqueous tension, but also with the further tendency of the dryer to become pasty or even liquid. For units such as the canisters in gas masks, pasty and liquid dryers cannot be used.

In the investigation undertaken, a catalyst for the conversion of carbon monoxide to carbon dioxide was employed at room temperature, with the gas stream at 50 per cent humidity, and with a rapid flow of gas. The use of various adsorbents, reactants, and dryers necessarily limits the space which the drying agent may occupy in a unit which shall be of a convenient size for safety and rescue work. With this in mind, the life of the drying agent was based on its ability to insure complete conversion of the carbon monoxide to carbon dioxide, with the particular catalyst concerned, in low-temperature conversion.

A catalyst sufficiently active to oxidize completely the carbon monoxide present in the gas at temperatures as low as 0° C. was found to be very sensitive to water vapor. The activity of this catalyst was decreased by 5 per cent when 1 per cent of its weight of water was adsorbed, and it became completely inactive when it had adsorbed 2.5 per cent of its weight of water. The above characteristics of the catalyst suggested its use for the determination of the capacity of drying agents.

The catalyst was intended for use in a carbon monoxide

gas-mask canister whose volume is limited by practical considerations, such as weight and breathing resistance. The space occupied by the drying agent was 150 cc. One tenth of this volume was used in the following tests.

A drying agent had to satisfy two requirements before its capacity was determined: it has to be granular in form in order to have low resistance to gas flow; also no noxious gases should be eliminated when water was adsorbed.

As has been intimated, the above requirements eliminate all liquid drying agents commonly used, as sulfuric or phosphoric acids, as well as materials which react with water with the subsequent evolution of a gas or vapor—i. e., a calcium carbide. Phosphorus pentoxide cannot be used, as it has a high initial resistance to gas flow which rapidly increases with the absorption of water vapor.

METHOD OF TESTING

The method used in testing the capacity of the drying agents was as follows: 15 cc. of the drying agent of 12–14 mesh were placed in an upright glass tube, 3 cm. in diameter, and the catalyst placed above it, a wire screen disk separating the two materials. Air 50 per cent saturated with water vapor at 20° C., containing 1 per cent of carbon monoxide by volume, was passed through the tube at 200 liters per hour. A carbon monoxide indicator sensitive to 0.01 per cent of carbon monoxide was used to determine the presence of carbon monoxide in the effluent gas. Twenty cubic centimeters of catalyst granules of 12–14 mesh were used in all tests. The capacity of the drying agent was measured by the time required to decrease the activity of the catalyst from 100 to 95 per cent. This 5 per cent decrease in activity meant that the dryer had permitted 0.17 gram of water vapor, which is 1 per cent of the catalyst weight, to escape and be adsorbed by the catalyst.

The relative humidity of the gas was controlled by passing it through two bottles of dilute sulfuric acid placed in series, the vapor pressure of water vapor over the acid being 13.2 mm. of mercury at 20° C.

At 200 liters per hour, the barometric pressure being 746.0 mm. of mercury, the volume of water vapor in the gas is 3.54 liters per hour, which is equivalent to 3.2 liters per hour at standard conditions, or 0.043 gram of water per minute. Since 4 minutes are required to deliver 0.17 gram of water, the

time when the dryer failed, as determined by experimentation, was reduced by 4 minutes, thus giving the actual life of the drying agent.

All drying agents tested were dehydrated at 400° C. under a total pressure of 20 mm. of mercury, with the exception of aluminum oxide and magnesium perchlorate. Aluminum oxide was dehydrated by heating to 1000° C. for 6 hours, magnesium perchlorate by gradually heating to 200° C. under a total pressure of 5 mm. of mercury.

TABLE I. CAPACITY OF DRYING AGENTS

Drying Agent	LIFE	WT. OF WATER	WT. OF MATE-	WATER
	Minutes	Absorbed Grams	RIAL OCCUPY- ING 15 CC. Grams	Absorbed %
Al ₂ O ₃	71	3.04	11.2	27.2
Mg(ClO ₄) ₂	56	2.40	7.5	32.0
CaCl ₂	56	2.40	11.0	21.8
BaO	26	1.11	30.0	3.7
CaCl ₂ , soda lime (50% each)	20	0.86	9.5	9.05
BaO ₂	16	0.69	27.0	2.6
Al ₂ (SO ₄) ₃	13	0.56	7.4	7.6
NaOH pellets	6	0.258	15.2	1.7
Na ₂ SO ₄	4	0.172	11.6	1.5
MgCl ₂	2	0.086	7.8	1.1
MgSO ₄	1	0.043	8.3	0.52
CaO	1	0.043	21.2	0.21

COMPARATIVE CAPACITIES OF VARIOUS DRYING AGENTS

Of the twelve drying agents tested in the above manner, only three were able to protect the catalyst for a minimum of 1 hour. Some of the drying agents permitted a small amount

of water vapor to escape from the start, the amount increasing as the material became hydrated. Calcium chloride, calcium oxide, and sodium hydroxide belong to this class. Others completely absorbed the water vapor up to a certain point, and then broke sharply, causing a rapid decrease in the activity of the catalyst. Magnesium perchlorate, aluminum oxide, sodium sulfate, barium oxide, and barium peroxide belong to this group.

Table I contains the experimental data, 15 cc. of drying agent and 20 cc. of catalyst being used in each test.

The significant value in this table is the weight of water absorbed by a definite volume of drying agent. Aluminum oxide absorbed the most water; next were calcium chloride and magnesium perchlorate. The others had relatively poor capacity.

It is of interest to observe that calcium chloride and magnesium perchlorate have the same capacity for water, although calcium chloride has a higher vapor pressure than magnesium perchlorate. The important difference in their behavior is that calcium chloride permits a small but measurable amount of water vapor to escape from the start, whereas magnesium perchlorate completely dries the gas until its capacity is reached.

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Direct Gravimetric Determination of Sodium in Commercial Aluminum

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THE magnesium uranyl acetate method for sodium is capable of giving satisfactory quantitative results when minute quantities of the element are present (1), and aluminum does not interfere with the determination (3). Since sodium is sometimes present as an impurity in aluminum, it was thought desirable to ascertain whether or not this method could be applied directly for estimating the percentage of this impurity in the commercial metal, and thus avoid difficulties inherent in any method based upon the preliminary separation of the sodium from the aluminum and other components of this material.

The samples for the experiments were furnished through the courtesy of the Research Laboratories of the Aluminum Company of America.

As the result of certain preliminary trials, the procedure followed was first to dissolve the weighed sample of drillings in the minimum possible amount of dilute hydrochloric acid, using a silica dish for this purpose. After dilution with water, the solution was filtered and the filtrate was concentrated to the smallest possible volume in a Pyrex flask, usually until hydrated aluminum chloride just started to separate. Then 100 cc. of magnesium uranyl acetate reagent were added and the determination completed as detailed elsewhere (2, 3). Apparently the various other impurities in the particular samples examined caused no interference. Precipitates were examined for silica with a view to applying a correction, but the amount present was always found to be insignificant. There was no reason to suspect that metallic impurities would cause error, and no evidence was found that they did.

With a sample of comparatively high sodium content the method proved quite satisfactory. As the results in Table I

show, the individual determinations checked well with each other and with the value for the sodium content of this particular material as determined in the laboratories of the Aluminum Company of America by their procedures. With a sample of somewhat lower sodium content, however, considerable difficulty was experienced in reducing the solution volume of the necessarily larger sample down to the point required for obtaining correct values by this method. The irregular results obtained in the second group of determinations reflect this difficulty. Even the use of a more concentrated reagent and the addition of this to larger volumes of solution, in this case 10 to 12 cc., as recommended in a recent paper (1), failed to produce entirely acceptable results. The last three values in the table were obtained in this manner.

TABLE I. DIRECT DETERMINATION OF SODIUM IN COMMERCIAL ALUMINUM

SAMPLE	WT. OF SAMPLE TAKEN	WT. OF PPT. FOUND	SODIUM FOUND		STATED VALUE
	Grams	Gram	To 3rd decimal	To 2nd decimal	
A	0.750	0.0183	0.037	0.04	0.04
	1.000	0.0230	0.035	0.04	
	1.500	0.0367	0.037	0.04	
			Av. 0.036	0.04	
B	2.000	0.0114	0.009	0.01	0.009
	2.000	0.0204	0.016	0.02	
	2.000	0.0171	0.013	0.01	
	2.000	0.0185	0.014	0.01	
	2.000	0.0095	0.007	0.01	
	2.000	0.0190	0.015	0.02	
B			Av. 0.012	0.01	0.009
	2.000	0.0115	0.009	0.01	
	2.000	0.0107	0.008	0.01	
	2.000	0.0173	0.013	0.01	
			Av. 0.010	0.01	

In general, it was apparent from the experiments that the amount of sodium in sample B represented the lowest possible percentage that could be estimated by this procedure, and that even in this case the results were not very satisfactory. It is recommended, therefore, that this method be applied only to the determination of sodium in metallic aluminum when the percentage of this impurity is greater than 0.01 per cent.

When this is the case, the above simple procedure is capable of yielding good results.

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RECEIVED February 27, 1932.

Construction of Accurate Air Separator

PAUL S. ROLLER, U. S. Bureau of Mines, New Brunswick, N. J.

THE author has previously described (1) a new type of air separator holding a charge of 600 cc. of powder and capable of effecting a particle-size separation into successive fractions beginning with 0-3 or 0-5 microns. Operations with this apparatus were at the time confined chiefly to Portland cement and pulverized anhydrite.

Recently there has been occasion to fractionate a gypsum powder that had been ground very fine in a pebble mill. In making a 0-5 micron cut on this material the rate of separation was found to be unusually low compared to the corresponding anhydrite fraction, even when allowing for the smaller rate of air flow due to the lower density of gypsum (2.32 as against 2.98). With the anhydrite the rate at which 0-5 micron particles collected in the felt filter bag, averaged over the first hour and a half, was 27 grams per hour; with the gypsum, however, the rate was only 3.3 grams per hour.

The difference was attributed to suspension and adherence of the soft fine gypsum particles in the lower conical portion of the 60.8-cm. (24-inch) settling chamber used. To counteract this condition, it was decided to tap the conical portion automatically. When this was done the 0-5 micron gypsum fraction separated out much more rapidly; the rate, averaged over the first hour and a half, being 16 grams per hour as against 3.3 grams per hour without tapping—i. e., the increase in rate was fivefold.

Besides greatly augmenting the rate of separation, the automatic tapper also increases the homogeneity of a given fraction. To understand how this comes about, it is recalled that in a given fractionation the particles that are blown over progressively increase in size with time. At the end point, corresponding to a definite rate of separation, which depends upon air flow and particle size and may be as high as 10 or 12 grams per hour, the particle sizes are in the boundary between the given fraction and the next succeeding fraction. If the fractionation is prolonged beyond the end point, the particle sizes will increase to a maximum value 1.41 times the theoretical maximum given by Stokes' law. This is because the maximum velocity at the center of the vertical chamber is by Poiseuille's law twice the mean velocity. Automatic tapping of the settling chamber renders the succession of particle sizes blown over more uniform, so that at the end point the number of particles which are greater or smaller than the theoretical maximum in size are reduced to a minimum. This result is particularly important at the higher rates of air flow.

Because of the pronounced increase in rate of separation and greater homogeneity of the fractions, not only for gypsum but also as observed for all other powders, the automatic tapper is now used as a standard adjunct to the air separator previously described (1).

The construction and method of mounting the automatic tapper, *I*, are shown in Figure 1. The oscillations of the U-tube, *C*, about bearing *B* impart the required motion to the tapper. The latter consists of three leaves, clipped to-

gether, of 0.8-mm. ($1/32$ -inch) spring steel about 4.5 cm. (1.75 inches) wide and 30.5 cm. (12 inches) high. At the upper end is a wooden hammer head weighted with lead so as to give an optimum blow. At the lower end the tapper is clamped in cantilever fashion to an L-shaped bracket which moves along a slotted horizontal plate. The latter is rigidly attached to the U-bend by means of uprights. The

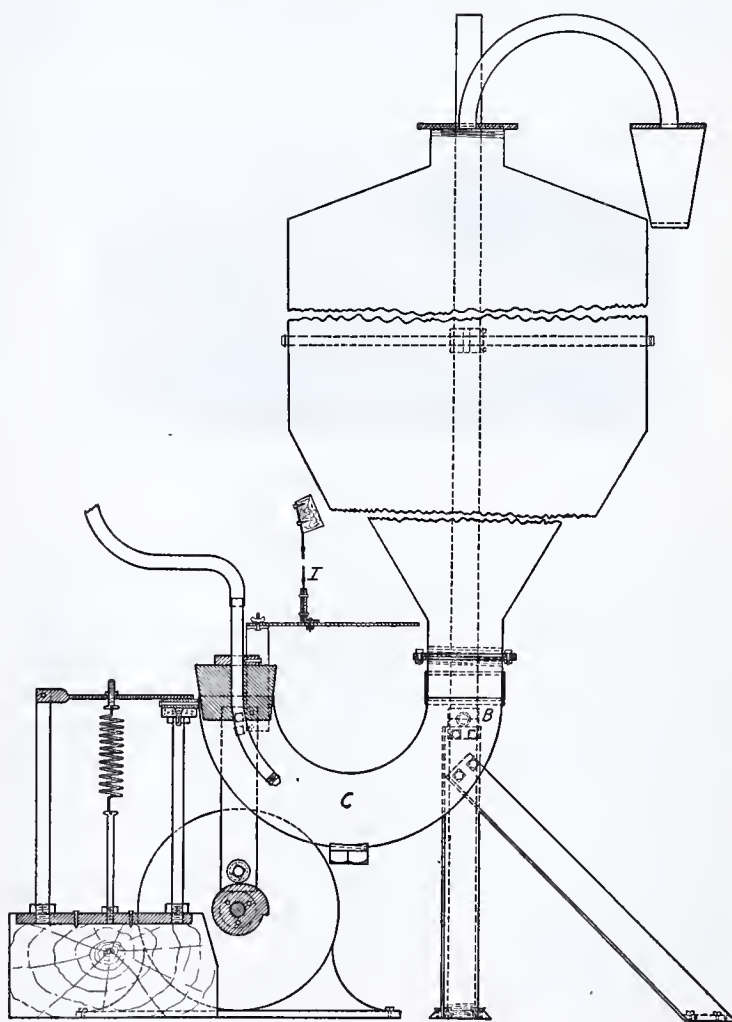


FIGURE 1. AIR SEPARATOR, VERTICAL SECTION

tapper is brought into position for maximum impact by moving it along the two slots in the horizontal plate, and is fastened in place on the horizontal plate by means of washers and wing nuts that screw onto bracket studs projecting through the slots.

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RECEIVED February 23, 1932. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

Apparatus for Reactions in Liquid Phase at Elevated Temperatures and Pressures

HOMER ADKINS, University of Wisconsin, Madison, Wis.

AN APPARATUS considered most satisfactory for laboratory use in carrying out reactions involving the agitation of a liquid and solid in the presence of a gas at temperatures and pressures above the normal (1) is pictured in Figure 1. It is convenient to describe this equipment under five heads—i. e., bomb, liner, gas inlet, heater, and shaker assemblies.

BOMB ASSEMBLY

A photograph of the bomb assembly and its parts is reproduced in Figure 2, and a cross-sectional diagram shown in Figure 3. All parts were made from a special steel S. A. E. No. 6140, obtained from the Crucible Steel Company of America, 17 East 42nd Street, New York, N. Y. This type of steel has the following analysis: carbon, 0.35 to 0.45;

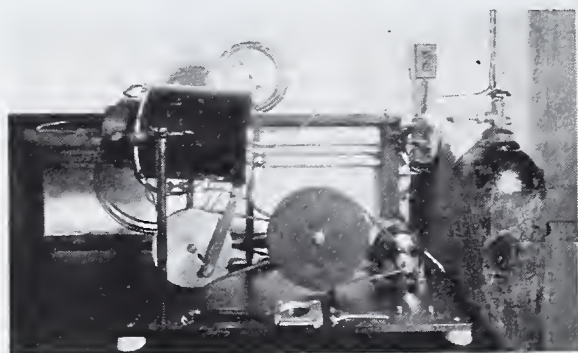


FIGURE 1. APPARATUS FOR REACTION UNDER PRESSURE

manganese, 0.50 to 0.80; chromium, 0.80 to 1.10; vanadium, 0.15 to 0.18; phosphorus (max.), 0.04; and sulfur (max.), 0.04. The bomb assembly is as follows:

The bomb proper is 19.6 cm. (7.7 inches) in length and 10.2 cm. (4 inches) in diameter, except at the threads where the diameter is larger to the extent of the depth of the threads. The chamber is 16.5 cm. (6.5 inches) in depth and 6.5 cm. ($2\frac{9}{16}$ inches) in diameter. The bomb is threaded at the top for 3.8 cm. (1.5 inches) with threads of the "acme" type, four to 2.54 cm. (1 inch). Threads eight to 2.54 cm. (1 inch) of the "E" type may also be used. The upper end of the bomb is machined smooth except for a channel 7.6 cm. (3 inches) in diameter, 1.3 mm. ($\frac{1}{20}$ inch) in depth, and 1.3 mm. ($\frac{1}{20}$ inch) in width. Two holes 1 cm. ($\frac{3}{8}$ inch) deep and 8 cm. ($3\frac{1}{3}$ inches) apart are bored in the bottom of the bomb so that it may be set on lugs in a base plate and so held while the cap screws in the bomb-head cover are tightened.

The bomb head is 10.2 cm. (4 inches) in diameter and 1.4 cm. ($\frac{9}{16}$ inch) thick. The boss is 3.2 cm. (1.25 inches) in height, and 5.4 cm. ($2\frac{1}{8}$ inches) in diameter. The thermocouple well is bored out of a steel rod 12.8 cm. (5 inches) in length and 1 cm. ($\frac{3}{8}$ inch) in diameter. Thermocouple wells are also readily made from 1.4 by 0.47 cm. ($\frac{9}{16}$ by $\frac{3}{16}$ inch) high-pressure tubing welded at one end. It is screwed into the bomb head to a depth 1.6 cm. ($\frac{5}{8}$ inch) against a copper gasket. The chamber in the thermocouple well and the corresponding opening in the bomb head is 4.7 mm. ($\frac{3}{16}$ inch) in diameter. If a thermometer is to be used, the diameter of the well should be increased to 16 by 8 mm. ($\frac{5}{8}$ by $\frac{5}{16}$ inch).

The thermocouple well is set 8 mm. ($\frac{5}{16}$ inch) off center. The inlet for the gas line is the standard one for use with 6.4 by 3.2 mm. ($\frac{1}{4}$ by $\frac{1}{8}$ inch) tubing. The opening from the chamber through the bomb head to the connection for the gas line is 3.2 mm. ($\frac{1}{8}$ inch) in diameter. The lower surface of the bomb head is machined smooth except for a groove similar to that on the top of the bomb and for a recess 0.8 mm. ($\frac{1}{32}$ inch) in depth and 6.4 mm. (0.25 inch) in width which holds the copper gasket. The bomb head is protected from the cap screws in the bomb-head cover by interposing a brass or steel plate 6.4 mm. (0.25 inch) in thickness and 9.9 cm. ($3\frac{7}{8}$ inches) in diameter with a circular opening in the center for the boss of the bomb head. The copper gasket is made from a copper sheet 3.2 mm. ($\frac{1}{8}$ inch) in thickness. It is 8.3 cm. (3.26 inches) outside diameter and 7 cm. (2.75 inches) inside diameter, and is therefore 6.4 mm. (0.25 inch) in width and fits into the recess provided for it in the bomb head. Lead gaskets from 3.2 mm. ($\frac{1}{8}$ inch) sheet lead and cut with an outside diameter of 9.9 cm. ($3\frac{7}{8}$ inches) and an inside diameter of 6 cm. ($2\frac{3}{8}$ inches) may ordinarily be used in place of copper.

The bomb-head cover is 12.7 cm. (5 inches) in diameter and 8.6 cm. ($3\frac{3}{8}$ inches) in height. The thread recess is 6.3 cm. (2.5 inches) deep. The opening in the bomb-head cover for the boss of the bomb head is just over 5.4 cm. ($2\frac{1}{8}$ inches) in diameter. The bomb-head cover carries eight square-headed cap screws 12.7 mm. (0.5 inch) in diameter, 3.8 cm. (1.5 inches) in length, thirteen threads to 2.54 cm. (1 inch). These are equally spaced on a circle 8 cm. ($3\frac{1}{8}$ inches) in diameter. Three holes 12.7 mm. (0.5 inch) in diameter and depth are bored at equal intervals in the side near the top of the bomb-head cover.

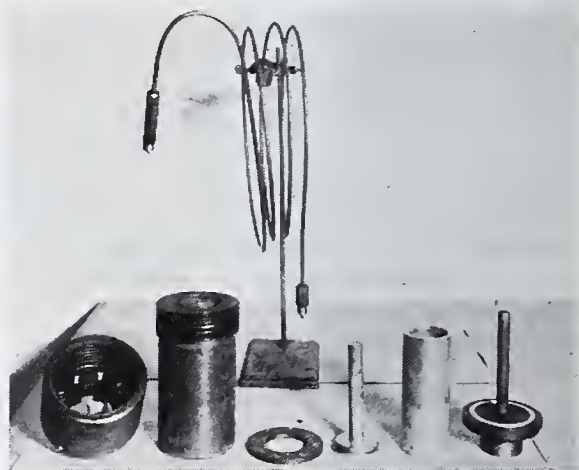


FIGURE 2. STEEL SPIRAL AND PARTS OF BOMB AND LINER

A bomb having about five times the capacity of the one described above but having essentially the same construction was made for us by the American Instrument Company, 774 Girard Street, Washington, D. C. This bomb is 12.5 cm. ($4\frac{15}{16}$ inches) in diameter, 37.5 cm. (14.75 inches) in length, and the chamber is 8.4 by 33.7 cm. (3.3 by 13.25 inches). The bomb head is 10.5 cm. ($4\frac{1}{8}$ inches) in diameter, 1.4 cm. (0.5 inch) thick, with a boss 5.1 cm. (2 inches) in diameter

and 5.5 cm. ($2\frac{1}{8}$ inches) high. The bomb head cover is 15.2 cm. (6 inches) in diameter and 10.5 cm. ($4\frac{1}{8}$ inches) high. The bomb and bomb-head cover are threaded for 6.4 cm. (2.5 inches) with "E" type threads, eight to 2.54 cm. (1 inch). There is an offset 11 by 19 mm. ($\frac{1}{25}$ by $\frac{3}{4}$ inch) just above the threads in the cover. The twelve 32 by 12.7 mm. (1.25 by 0.5 inch) cap screws extend through steel for 16 mm. ($\frac{5}{8}$ inch) to press against the steel thrust plate, which in turn is forced against the bomb head. The copper gasket is 9.6 cm. (3.77 inches) outside and 9.2 cm. (3.62 inches) inside diameter, and 1.6 mm. ($\frac{1}{16}$ inch) thick.

LINER OR REACTION CONTAINER

This is made of standard brass tubing having a wall thickness of approximately 1.6 mm. ($\frac{1}{16}$ inch). A reproduction of a photograph of one of these liners is shown in Figure 2 and a cross-sectional diagram in Figure 4. (The closure of the liner pictured in Figure 2 is somewhat different from that recommended and shown in Figure 4.) For the smaller bomb described above, the liner is made from brass tubing 6.4 cm. (2.5 inches) outside diameter, and for the larger bomb from 8.3-cm. (3.25-inch) tubing. The over-all length of the liner complete should be approximately 6.4 mm. (0.25 inch) less than the depth of the chamber in the bomb. The bottom of the liner is a brass plate 3.2 mm. ($\frac{1}{8}$ inch) thick, silver-soldered into place. The top of the liner is a brass plate 9.6 mm. ($\frac{3}{8}$ inch) thick, which carries a well for the thermocouple well of the bomb head. The top plate is screwed down against a lead gasket. A piece of brass of the shape indicated in the drawing is placed inside the larger brass tube and attached to it with silver solder. The ledge for the gasket is 6.4 mm. (0.25 inch) wide and grooved as described for the bomb and bomb head. The threads are eighteen to 2.54 cm. (1 inch). A 1.6-mm. ($\frac{1}{16}$ -inch) hole is located in the side half way from the top to the bottom of the liner, through which gas may enter the reaction space. The well in the liner is of brass tubing 0.8 mm. ($\frac{1}{32}$ inch) in wall thickness, and is closed at the bottom. It is screwed into and soldered to the top of the liner so that it is 8 mm. ($\frac{5}{16}$ inch) off center. The tubing may be either 19 mm. (0.75 inch) or 12.7 mm. (0.5 inch) inside diameter, depending upon the diameter of the well in the bomb head. Two holes 6.3 mm. (0.25 inch) deep and 4.8 mm. ($\frac{3}{16}$ inch) in diameter are located in the head of the liner to permit the insertion of the lugs of a wrench to be used in opening and closing the liner. The capacity of the liner for the smaller bomb is approximately 150 ml., whereas the larger accommodates 750 ml.

GAS INLET ASSEMBLY

The essential parts of this assembly are a spiral of steel tubing, a gage, two valves, and such nipples and connections as are necessary for attaching these to the hydrogen tank, to the bomb, and to each other. Drawn molybdenum steel tubing 6.4 mm. (0.25 inch) outside diameter by 3.2 mm. ($\frac{1}{8}$ inch) inside diameter is used for the spiral and nipples. A suitable arrangement of the spiral is shown in Figure 2. A piece 2.3 meters (7 feet) or more in length may be made into a spiral by wrapping it around a gas tank 15 cm. (6 inches) in diameter. The spiral will then spring out to a diameter of approximately 23 cm. (9 inches). The spiral is washed out with hydrochloric acid and then with acetone before it is put into use. This washing is to remove scale, etc., loosened during the bending process and which may later accumulate at one point and close the opening.

The dimensions and type of connection will necessarily depend upon the valves, etc., which are to be used. The standard connection for 6.4 by 3.2 mm. ($\frac{1}{4}$ by $\frac{1}{8}$ inch) tubing has been described (2). All other connections should be made gas-tight with the aid of lead or copper gaskets.

The gage is of the hydraulic type, 15.2-cm. (6-inch) iron case, with 12.7-mm. (0.5-inch) straight pipe thread connection, purchased from the United States Gauge Company. It is calibrated for pressures up to 340 atmospheres (5000 pounds per square inch). The valves supplied by the American Instrument Company are perhaps the most satisfactory, although the much cheaper Hoke valves have given excellent service. If these latter are used, care must be taken to insert them in the system so that the arrows on them are pointing away from the bomb system. This is necessary because these cheaper

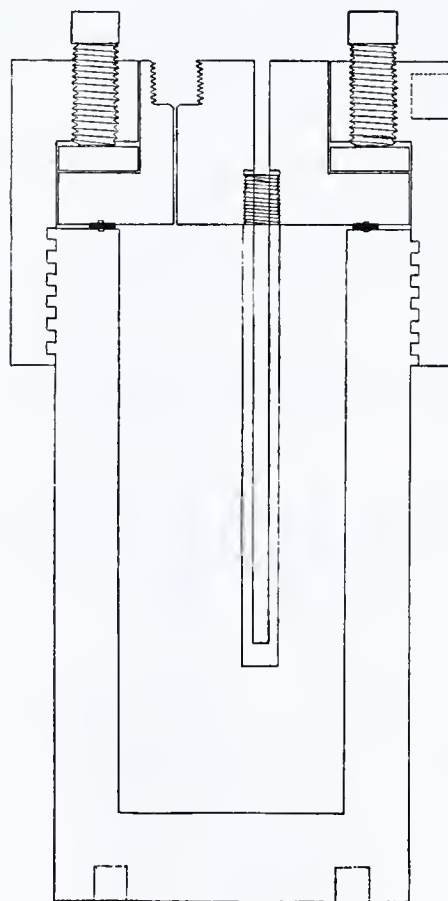


FIGURE 3. CROSS SECTION OF BOMB

valves hold gas under pressure satisfactorily only when they are *closed*, and then only on the side of the valve on which the gas is *not* against the valve packing.

In the set-up shown in Figure 1, the order of parts beginning at the hydrogen tank is (1) an adapter, (2) a collar, (3) a Hoke valve, (4) a tee, (5) a 2-foot length of steel tubing, (6) a tee, and (7) a spiral of steel tubing. A valve and the gage are screwed into the side openings in the two tees. The tee for the gage is attached to the base plate of the shaker assembly by a 1.9-cm. (0.75-inch) steel rod. If the American Instrument Company type of valve is used, a short nipple replaces the collar, the first tee is eliminated, the second tee is changed to a four-way connection, and the outlet valve is connected to it by a short nipple.

HEATER ASSEMBLY

The heating unit is made of two spirals of No. 18 nichrome wire connected in parallel and each carrying approximately 3.5 amperes on a 110-volt current. These spirals are made by winding a 22.9-meter (75-foot) length of the nichrome wire on a 1-cm. ($\frac{3}{8}$ -inch) steel rod which is rotated in a lathe. The spiral is then removed from the rod and pulled out to a length of about 1.5 meters. A hollow cylinder of 0.8-mm. ($\frac{1}{32}$ -inch) sheet iron is then made of such a diameter as to slip over the bomb as far as the bomb-head cover. The sheet iron is covered with a layer of asbestos paper and the spirals of

nichrome wire wound over it. The spirals are kept separate from each other by interposing asbestos between them. The terminals of the spirals are fastened to binding posts on a circular piece of transite attached to one end of the sheet-iron cylinder. The spirals are covered with two layers of asbestos paper and a second sheet-iron cylinder slipped over the covered spirals. Such heating units have been in almost daily use for 2 or 3 years and have given entire satisfaction. When carrying the maximum of 7 amperes, the unit will heat the smaller bomb referred to above to 100° C. in 30 minutes, to 200° C. in 60 minutes, and to 250° C. in 80 minutes. The heating unit for the larger bomb contains two spirals of No. 18 nichrome wire 13.4 meters (44 feet) in length, each carrying 6 amperes. This unit heats the bomb to 200° C. in 87 minutes and to 250° C. in 120 minutes.

The electrical circuit connected to the heater should include an ammeter and a rheostat for reducing the current passing through the heater after the bomb has reached the desired temperature. A current of 4.5 amperes is more than enough to keep the smaller bomb at 250° C. if the heater is suitably insulated. The temperature of the bomb may be controlled by means of the rheostat. However, Leeds and Northrup potentiometer controllers with a suitable relay have always been used in this laboratory with or without an indicating or recording attachment.



FIGURE 4. CROSS SECTION OF LINER

SHAKER ASSEMBLY

This assembly is intended to rock the bomb through an angle of approximately 30 degrees—i. e., the bomb placed on its side is rocked so one end is alternately 15 degrees above and 15 degrees below the horizontal. The rate of oscillation is from 35 to 43 per minute. The movement is obtained from a 0.05 h. p. electric motor having a speed of 1725 revolutions per minute and bearing a pulley 2.2 cm. ($\frac{7}{8}$ inch) in diameter. A belt from this pulley passes to a free running pulley 22.7 cm. (9 inches) in diameter, which has a pulley 2.2 cm. ($\frac{7}{8}$ inch) in diameter attached to it. A second belt passes from this smaller pulley to a 17.2-cm. (6.75-inch) slotted pulley. This slotted pulley is attached by a driving arm to the receptacle which holds the bomb heater, which in turn holds the bomb. The slot in the pulley makes it possible to adjust the stroke of the driving arm and hence to control to a certain extent the violence of the agitation of the reactants. This may be further modified by changes in the size of the pulley on the motor shaft.

It seems unnecessary to describe in any considerable detail the construction of the shaker, since it may be modified in so many ways. The heater receptacle should be so constructed as to minimize heat losses. The one illustrated has a layer of insulating material approximately 25 mm. (1 inch) thick about the heater. All parts of the shaker shown in Figure 1 are mounted on a 12.7-mm. (0.5-inch) steel base plate. It also carries two lugs for holding the bomb in position while it is being opened and closed, as well as a device for holding the liner while its head is being screwed down or loosened. The bearings for the pulleys and the shaker are mounted on five 1.9-cm. (0.75-inch) steel rods screwed into the base plate. The bearings are attached to the upright rods by means of the larger size muffs ordinarily used on ring stands. If, with the bomb in place and the spiral attached, the shaker is not well balanced, then a weight should be so added that the shaker

moves up and down with the expenditure of the minimum of effort.

OPERATION OF EQUIPMENT

The catalyst and reactant(s) with or without a solvent are placed in the liner and the head tightened down snugly. The liner is then placed in the bomb while the latter is resting on the lugs provided in the base plate. Care must be taken to note the location with respect to the bomb of the hole in the side of the liner. The bomb head (with the copper gasket in the recess provided for it) is placed in position with the thermocouple well extending down into the well in the liner. (The wells were made "off center" so that the liner cannot turn in the bomb after the bomb is closed.) The thrust plate is then placed on the bomb head and the bomb-head cover screwed down (to within a fraction of a turn) as far as it will go. The cap screws are then turned down. Each screw should be turned down only a little at a time, the order of tightening being in general

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      3
    5   8
  1     2
    7   6
      4
  
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The bomb is placed in the shaker, care being taken that the hole in the side of the liner is uppermost. The gas line is screwed in and tightened, the bomb being held from turning by a rod inserted into one of the holes in the side of the bomb-head cover. Gas is allowed to flow into the bomb from the tank slowly until a little more than the desired pressure is registered by the gage. The valve between the tank and the bomb is then closed and the shaker started. There will be a slow drop in pressure for a few minutes, but after 5 minutes there should be no further drop. If there is a further drop in pressure, all connections (valve stems, etc.) should be tested with a soap solution. If the leak is at the gasket, then the cap screws may be further tightened. If the leak persists, there is probably a defect in the gasket. This may sometimes be remedied by simply opening and closing the bomb. If this is not effective, a new gasket should be used. When no drop in pressure has been noted on the gage for an interval of 5 or 10 minutes, the heater may be turned on. Shortly before the temperature of the bomb reaches the desired value, the current passing through the heater should be reduced to such a value as will not permit the bomb to go much higher in temperature.

As the bomb is heated, the pressure as indicated by the gage will rise approximately in accord with the temperature expressed on the absolute scale, the amount of the deviation being mainly a function of the compounds in the liner. The deviations will become considerable as the critical temperature of any compound is reached (190° to 200° C. for ether, 245° to 250° C. for ethanol). In general, however, the discrepancy between the calculated and observed pressure is due to the absorption of hydrogen. Thus a comparison of the calculated and observed pressures at various temperatures will indicate the point at which hydrogenation begins.

The relationship between the drop in pressure, indicated by the gage and the amount of hydrogen absorbed should be determined by hydrogenating some compound such as acetone which is smoothly and quantitatively hydrogenated to a single product. For a smaller bomb described with 100 ml. of liquid in the liner, the pressure drop for one mole of hydrogen will approximate 1250 pounds per square inch (85 atmospheres) measured at 22° C., or 1740 pounds (119 atmospheres) measured at 150° C. For the larger bomb with 500 ml. of liquid in the liner, the pressure drop per mole of hydrogen will

approximate 275 pounds per square inch (19 atmospheres) measured at 22° C. The drop in pressure per mole of hydrogen is a linear function of the amount of liquid in the bomb, the slope of the line being dependent upon the space for gas in the bomb.

The extent of hydrogenation may be approximated by observing the drop in pressure at the temperature of hydrogenation. However, such a value is in general much less accurate than that based upon a comparison made at room temperature between the pressure before the bomb was heated up with that observed after the contents of the bomb have cooled to the original temperature.

When the desired reaction is complete, the bomb may be pulled partially out of the heater in order to facilitate its cooling. Often it is advantageous then to place a water jacket around the bomb so that it may be more rapidly cooled to room temperature.

When the bomb has cooled to room temperature, the pressure is *slowly* released by allowing the gas to escape through the outlet valve. The gas inlet is disconnected from the bomb, the latter removed from the heater, the cap screws loosened, and the bomb-head cover unscrewed. The head should then be gently loosened by tapping and attempting to rotate it. (If an attempt is made to lift it directly from the bomb, the gasket will probably be ruined.) The liner is then removed, opened, and the catalyst removed by filtering through a sintered glass filter. The bomb and liner may be washed out with a suitable solvent and this solution added to the reaction mixture. In many cases it is advantageous to centrifuge the mixture before attempting to filter off the catalyst.

PRECAUTIONS

The smaller bomb described above is intended for use at pressures up to 175 atmospheres and temperatures up to 250° C., although the factor of safety under these conditions is several hundred per cent. The larger bomb is intended for use at pressures up to 400 atmospheres. The pressure of the hydrogen in the usual type of commercial cylinders is approximately 135 atmospheres, so that the maximum pressure obtainable (without the use of special equipment for compressing the gas) would be approximately 240 atmospheres at 250 C. A gage should only be used over the lower 60 per cent of its range, so that 200 atmospheres is approximately the maximum pressure that should be used with the equipment suggested. The gage is the weakest point in the system, and it is well to replace the glass in it with celluloid and to have it so located that it is not faced directly but is read by means of a mirror. The temperature of hydrogenation should be carefully watched, and if the reaction is proceeding too rapidly, the shaker should be stopped for a time.

ACKNOWLEDGMENT

The author's experience with the apparatus and technic for carrying out the reaction of organic compounds at temperatures up to 400° C. and pressures of several hundred atmospheres began in 1927 with apparatus purchased from the American Instrument Company. This equipment is still in use and it has never developed any fundamental defects. Since that time the bomb design, gaskets, etc., described in this paper have been developed as being more convenient and cheaper, and in general more satisfactory. The author is particularly indebted to W. H. Reynolds and Leopold Freedman of the American Instrument Company, and to Messrs. Hanson, Brockman, and Henke of the shops of the University of Wisconsin. The American Instrument Company have on the market an outfit for catalytic hydrogenation which includes the essential features of the unit described in

this paper. The Burgess-Parr Company of Moline, Ill., also have for sale an outfit patterned after the unit herein described.

LITERATURE CITED

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- (2) Ernst, *IND. ENG. CHEM.*, **18**, 664 (1926); Am. Instrument Co., *Bull.* 405 (1927); U. S. Dept. Agr., *Circ.* 61 (1929).

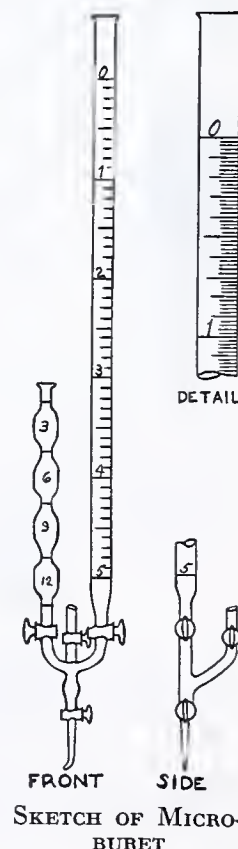
RECEIVED March 19, 1932.

A Modified Microburet

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SOME years ago the Department of Agricultural Chemistry became engaged in analyses necessitating the use of a microburet. Reference to several supply house catalogs at hand revealed only the Folin type available. One of these was purchased and put into use, but it did not meet the needs in a satisfactory manner. Consequently a buret was designed as illustrated in the accompanying sketch.

The advantage of this type of buret lies chiefly in its increased capacity without sacrificing any of the conveniences of the ordinary single-tube type. The short length of the graduated tube affords convenient reading throughout its entire range without undue elevation or lowering of the level of the eyes. For titration with small withdrawals of liquid, this part of the buret may be used exclusively if desired. When titrating from the graduated tube, the bulb side furnishes a convenient outlet for excess solution run into the buret from the stock bottle and adjusted to the zero graduation. However, when considerable quantities of solution are required, the bulb side is more suitable. When titrating from the bulb side, the titration is completed by manipulation of the lowest stopcock, the stopcock on the left remaining open. After the titration is finished, the stopcock on the right is opened and the liquid in the partially emptied bulb allowed to rise to the nearest graduation mark above. It may be noted that the zero graduation on the top bulb stands slightly below the level of the 3-ml. graduation on the uniform-bore tube. This permits the refilling of any one of the four bulbs on the left hand side with liquid drawn from the main tube on the right. The total quantity is then read off by adding to the volume of the emptied bulbs the volume withdrawn from the gradu-



ated tube. All titrations are best controlled by the use of the lowest stopcock.

This buret delivers approximately 26 drops per ml. and is suitable for work with blood and urine in addition to the more general analytical procedures. The graduation interval is 0.02 ml., but readings are easily possible to 0.01 ml. Because of the relatively small bore of the graduated tube, some time must be allowed for afterflow if the tube has been emptied rapidly and readings of greatest accuracy are desired. This seldom requires a total of more than 1.5 to 2 minutes, and ordinarily most of this drainage will have taken place during the time necessary for the withdrawal of the last few drops.

Two of these burets have been made at moderate cost by E. Machlett & Son of Long Island City, N. Y., the first of which has been in constant use over a period of 2 years. They are of rugged construction and excellent workmanship. The calibration is highly accurate, the volumes being adjusted well within the tolerances required by the U. S. Bureau

of Standards for measuring pipets. The approximate dimensions of the buret are as follows:

	Cm.
Total length.....	60
Length of graduated main tube from 0 to 5 ml.....	38
Height of side tube with bulbs.....	23
Distance from 5-ml. graduation to point of curved tip	15
Length of tip below stopcock.....	4
Diameter of graduated main tube (outside).....	0.8
Diameter of bulbs (outside).....	1.4
	Ml.
Total capacity.....	17
Capacity of graduated main tube.....	5
Capacity of single bulb.....	3
Subdivisions.....	0.02

These dimensions give a small unit convenient both for general laboratory use and for certain specialized procedures. Manipulation is rapid and easy, total capacity large, and accuracy adequate for exact measurements.

RECEIVED January 11, 1932. Published with the approval of the Director of the West Virginia Agricultural Experiment Station, as *Scientific Paper* 106.

Pressure Control with Automatic Liquid-Leveling Device

J. V. VAUGHEN, E. I. du Pont de Nemours & Co., Wilmington, Del.

THERE is often a need in the laboratory for a device which will automatically control liquid levels in the leveling bulbs of gasometers and combustion pipets and in mercury reservoirs in such a way as to give constant pressure or constant liquid flow.

Figure 1 represents a variation of the arrangement used by Stone (1) that has been used in this laboratory for maintaining a constant flow of mercury to displace liquids at a constant rate into a reaction vessel.

The mercury reservoir, C, is suspended by a suitable spring, B, which lifts the reservoir a distance equal to the fall in mercury level in the bulb when mercury flows out. The spring and reservoir are matched by measuring the elongation, X, of the spring with a load of 100 cc. of mercury. The appropriate diameter, D, of the reservoir is then calculated according to the formula

$$D = 2\sqrt{\frac{100}{X\pi}}$$

The reservoir is made of tubing of approximately this diameter, and further matching is accomplished by changing the length of the spring.

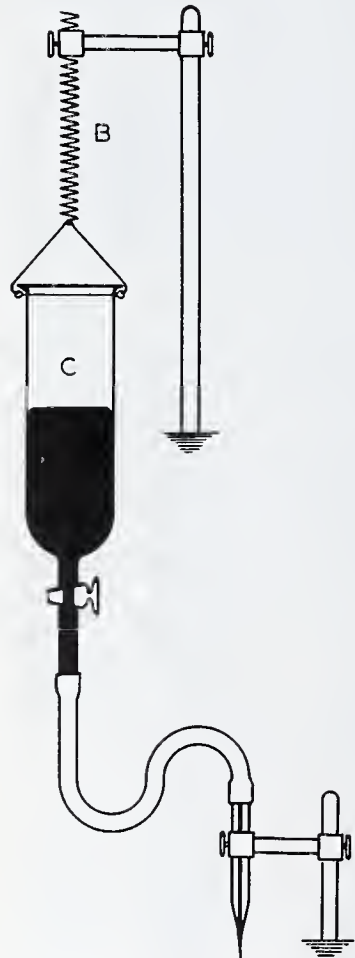


FIGURE 1. DIAGRAM OF LEVELING DEVICE

Brass springs have been found more suitable than steel ones, and they are generally made by winding No. 16 B. & S. brass wire on a 0.25-inch (0.62-cm.) mandrel. In one in-

stance two springs 27 cm. long were used together to support a mercury reservoir. Together these springs stretched 6.8 cm. for 100 cc. of mercury. The calculated diameter of the reservoir was 4.32 cm. The reservoir was made with a diameter of 4.5 cm. and further adjustment of the apparatus was accomplished by shortening the spring. A volume of 200 to 300 cc. of mercury could be emptied from the reservoir with a change in mercury level of less than 3 mm.

In applying this scheme to the maintenance of constant pressure in gasometers and combustion pipets with leveling bottles, the following equation gives the relationship between the radius, r, of the gasometer or combustion pipet, the radius, R, of the leveling bottle, and the elongation, X, of the spring, for a volume, V, of confining liquid:

$$X = \frac{V}{\pi r^2} + \frac{V}{\pi R^2}$$

In one instance a leveling bottle for a gas-combustion pipet was suspended by two springs 42 cm. long. They elongated 8.0 cm. with a load of 100 cc. of mercury. Since the diameter of the pipet was 4.8 cm., the leveling bulb should measure 7.2 cm.

LITERATURE CITED

- (1) Stone, *Engineering*, 100, 554 (1915).

RECEIVED February 16, 1932. Contribution 91 from the Experimental Station, E. I. du Pont de Nemours & Company.

WORLD POTASH PRODUCTION. According to the estimate of the general director of the Kaliwerke Aschersleben, reported to the Department of Commerce by the trade commissioner at Berlin, potash salts representing 1,457,400 metric tons of potash were produced in the world in 1931. In 1930 world production of potash was 2,018,000 tons, and in 1929, 2,118,000 tons. Germany is first in volume of potash produced, with 964,000 tons; France (Alsace) second with 340,000 tons; the United States third with 60,000 tons; and then Poland, Spain, Russia, in the order named. A decline from over 1,300,000 tons in 1930 is shown in German production, and a drop of 16 per cent for the first five months of 1932 over the corresponding period in 1931, in sales of German potash.

Recommended Specifications for Analytical Reagent Chemicals

Benzene, Cupric Acetate Normal ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$), Cupric Nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), Lead Subacetate, Phenolphthalein, Potassium Nitrate, Sodium Fluoride, Sodium Nitrite, Toluene, Xylene

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Committee on Analytical Reagents, American Chemical Society

THE specifications given below are intended to serve for reagents to be used in careful analytical work. The limits and tests are based on published work, on the experience of members of the committee in the examination of reagent chemicals on the market, and on studies of the tests made by members of the committee as the various items were considered. Suggestions for the improvement of the specifications will be welcomed by the committee.

In all the directions the acids and ammonium hydroxide referred to are of full strength unless dilution is specified; dilution indicated as (1 + 3) means 1 volume of the reagent or strong solution with 3 volumes of water; "water" means distilled water of a grade suitable for the test described; reagents used in making the tests are supposed to be of the grade recommended below or in previous publications (1-9) from the committee. Directions for the preparation of the ammonium molybdate solution are given under the test for phosphate in ammonium nitrate (3). A time of 5 minutes is to be allowed for the appearance of precipitates and before observation of color reactions, unless some other time is specified.

Blank tests must be made on water and all reagents used in the tests unless the directions provide for elimination of errors due to impurities. Solutions of samples must be filtered for tests in which insoluble matter would interfere.

BENZENE

REQUIREMENTS

Boiling Range—79.5° to 81° C.

Solidification Temperature—Not below 5.2° C.

Nonvolatile Matter—Not more than 0.001 per cent.

Substances Darkened by Sulfuric Acid—To pass test.

Thiophene—To pass test.

Sulfur Compounds (S)—Not more than 0.005 per cent.

TESTS

Boiling Range—When 100 cc. are subjected to the distillation test described in the U. S. Pharmacopeia, not less than 95 cc. should distil within the range indicated.

Solidification Temperature—When tested according to the method described in the U. S. Pharmacopeia, the temperature of solidification should not be below 5.2° C.

Nonvolatile Matter—Evaporate 115 cc. on the steam bath and dry at 105° to 110° C. for 30 minutes. The weight of the residue should not exceed 0.0010 gram.

Substances Darkened by Sulfuric Acid—Shake 25 cc. with 15 cc. of sulfuric acid for 15 to 20 seconds and allow to separate. Neither the benzene nor the acid should be darkened.

Thiophene—Add a few milligrams of isatin to the mixture of benzene and sulfuric acid from the preceding test, shake well, and allow to stand for 1 hour. The acid layer should not acquire a blue or green color.

Sulfur Compounds—Place 30 cc. of approximately 0.5 N alcoholic potassium hydroxide in an Erlenmeyer flask, add 6 cc. of the sample, and boil the mixture gently for 30 minutes under a reflux condenser. Detach the condenser, dilute with 50 cc. of water, and heat on the steam bath until the benzene and alcohol

are evaporated. Add 50 cc. of saturated bromine water and heat for 15 minutes longer. Transfer the solution to a beaker, neutralize with dilute hydrochloric acid (1 + 4), add an excess of 1 cc. of the acid, and concentrate to about 50 cc. Filter, if necessary, heat the filtrate to boiling, add 5 cc. of barium chloride solution, heat on the steam bath for 2 hours, and allow to stand overnight. If a precipitate is formed, filter, wash, and ignite. A blank should be run with the quantities of reagents used in the test and including filtration and ignition. The difference between the weights of ignited precipitates for the sample and for the blank should not be more than 0.0020 gram.

CUPRIC ACETATE NORMAL ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$)

REQUIREMENTS

Insoluble Matter—Not more than 0.010 per cent.

Chloride (Cl)—Not more than 0.003 per cent.

Sulfate (SO_4)—Not more than 0.010 per cent.

Alkali Salts—Not more than 0.20 per cent.

Iron (Fe)—Not more than 0.010 per cent.

Ammonium Sulfide Metals (other than Fe)—To pass test (limit about 0.01 per cent Ni).

TESTS

Insoluble Matter—Dissolve 10 grams in 150 cc. of water containing 1 cc. of glacial acetic acid and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash thoroughly, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0010 gram.

Chloride—Dissolve 1 gram in 20 cc. of water, add 1 cc. of nitric acid and 1 cc. of 0.1 N silver nitrate. Any turbidity should not be greater than is produced by 0.03 mg. of chloride ion in an equal volume of water containing the quantities of reagents used in the test.

Sulfate—To the filtrate from the test for insoluble matter add 5 cc. of glacial acetic acid, heat to boiling, add 5 cc. of 10 per cent barium chloride solution, and allow to stand overnight. Filter, wash, ignite, and weigh. The weight of the barium sulfate should not be more than 0.0025 gram greater than the weight obtained in a blank test with the same quantities of reagents and including filtration.

Alkali Salts—Dissolve 4 grams in about 190 cc. of water, add 2 cc. of sulfuric acid, heat to about 70° C., and pass in hydrogen sulfide until the copper is completely precipitated. Dilute to 200 cc. and filter. Evaporate 150 cc. of the filtrate to dryness, ignite, and weigh the residue. The weight of the residue should not exceed 0.0060 gram.

Iron—Warm the residue obtained from the test for alkali salts with 1 cc. of hydrochloric acid and 2 drops of nitric acid, and dilute to 15 cc. with water. Dilute 5 cc. of this solution with 15 cc. of water, and add 2 cc. of hydrochloric acid and 3 cc. of 10 per cent ammonium thiocyanate solution. Any red color should not be greater than is produced by 0.1 mg. of iron under the same conditions.

Ammonium Sulfide Metals, Other than Iron—To the remaining 10 cc. of the solution of the residue add a slight excess of ammonia, boil for 1 minute, filter, and wash with a small quantity of hot water. Dilute the filtrate and washings to 25 cc. Exactly neutralize 5 cc. of the filtrate and washings with dilute hydrochloric acid and dilute to 20 cc. Add 2 drops of ammonium hydroxide and 1 cc. of hydrogen sulfide water. The solution should not be darker than a standard prepared in the same way and containing 0.04 mg. of nickel.

CUPRIC NITRATE ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$)

REQUIREMENTS

Insoluble Matter—Not more than 0.010 per cent.
Chloride (Cl)—Not more than 0.002 per cent.
Sulfate (SO_4)—Not more than 0.01 per cent.
Alkali Salts—Not more than 0.05 per cent.
Iron (Fe)—Not more than 0.010 per cent.
Ammonium Sulfide Metals (other than Fe)—To pass test (limit about 0.01 per cent Ni).

TESTS

Insoluble Matter—Dissolve 10 grams in 100 cc. of water containing 0.5 cc. of nitric acid, and heat on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash thoroughly, and dry at 105° to 110° C. The weight of insoluble residue should not exceed 0.0010 gram.

Chloride—Dissolve 1 gram in 20 cc. of water and 1 cc. of nitric acid, filter if necessary, and add 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.02 mg. of chloride ion in an equal volume of water containing the quantities of reagents used in the test.

Sulfate—Dissolve 5 grams in 5 cc. of hot water, add 10 cc. of hydrochloric acid and evaporate to dryness on the steam bath, redissolve the residue in about 5 cc. of hot water, add 10 cc. of hydrochloric acid and reëvaporate to dryness. Dissolve the residue in 100 cc. of water, add 1 cc. of hydrochloric acid, and filter. Heat to boiling, add 5 cc. of 10 per cent barium chloride solution, and allow to stand overnight. If a precipitate is formed, filter, wash, and ignite. The weight of the precipitate should not be more than 0.0013 gram greater than the weight obtained in a blank test with the same quantities of reagents and including filtration.

Alkali Salts—Dissolve 4 grams in about 190 cc. of water, add 2 cc. of sulfuric acid, heat to about 70° C., and pass in hydrogen sulfide until the copper is completely precipitated. Dilute to 200 cc. and filter. Evaporate 150 cc. of the filtrate to dryness, and ignite and weigh the residue. The weight of the residue should not exceed 0.0015 gram.

Iron—Warm the residue obtained from the test for alkali salts with 1 cc. of hydrochloric acid and 2 drops of nitric acid, and dilute to 15 cc. with water. Dilute 5 cc. of this solution with 15 cc. of water. Add 2 cc. of hydrochloric acid and 3 cc. of 10 per cent ammonium thiocyanate solution. Any red color should not be deeper than is produced by 0.1 mg. of iron under the same conditions.

Ammonium Sulfide Metals, Other than Iron—To the remaining 10 cc. of the solution of the residue add a slight excess of ammonia, boil for 1 minute, filter, and wash with a small quantity of hot water. Dilute the filtrate and washings to 25 cc. Exactly neutralize 5 cc. of the filtrate and washings with dilute hydrochloric acid and dilute to 20 cc. Add 2 drops of ammonium hydroxide and 1 cc. of hydrogen sulfide water. The solution should not be darker than a standard prepared in the same way and containing 0.04 mg. of nickel.

LEAD SUBACETATE

REQUIREMENTS

Assay of Lead (Pb)—70 to 73 per cent.
Insoluble in Acetic Acid—Not more than 0.05 per cent.
Chloride (Cl)—Not more than 0.005 per cent.
Nitrate (NO_3)—To pass test (limit about 0.003 per cent).
Substances Not Precipitated by Hydrogen Sulfide—Not more than 0.30 per cent.
Copper (Cu)—To pass test (limit about 0.005 per cent).
Iron (Fe)—Not more than 0.005 per cent.

TESTS

Assay of Lead—Weigh accurately about 1 gram in a porcelain crucible, add about 0.5 cc. of sulfuric acid, and ignite to drive off the excess of acid. The weight of lead sulfate should correspond to between 70 and 73 per cent of lead.

Insoluble in Acetic Acid—Dissolve 6 grams in 100 cc. of water and 5 cc. of glacial acetic acid, and warm if necessary. If an insoluble residue remains, filter and wash until the washings are no longer darkened by hydrogen sulfide. Dry at 105° to 110° C. The weight of the residue should not exceed 0.0030 gram.

Chloride—Dissolve 1 gram in 10 cc. of water and add 1 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.05 mg. of chloride ion in an equal volume of solution containing the quantities of reagents used in the test.

Solution A—Dissolve 5 grams in 42 cc. of water and 3 cc. of glacial acetic acid, and add 5 cc. of sulfuric acid. After standing for about 10 minutes, filter the solution.

Nitrate—To 10 cc. of Solution A add 2 drops of indigo solution (1 in 1000) and 10 cc. of sulfuric acid. The blue color should not disappear in 5 minutes.

Substances Not Precipitated by Hydrogen Sulfide—Dilute 10 cc. of Solution A with water to 100 cc., pass hydrogen sulfide to precipitate all the lead, and filter. Evaporate 50 cc. of the filtrate to dryness and ignite gently. The weight of the residue should not exceed 0.0015 gram.

Copper—To 25 cc. of Solution A, add ammonium hydroxide until barely alkaline, heat on the steam bath for 10 minutes, and add 10 cc. of ammonium hydroxide. No blue color should be observed when the solution is compared with an equal volume of water in a Nessler tube.

Iron—Dissolve 2 grams in a few cc. of water, add 2 cc. of sulfuric acid, and heat to fumes of sulfuric acid. Allow to cool, dilute with water to 30 cc., and filter. To 15 cc. of the filtrate add 2 cc. of hydrochloric acid and 3 cc. of 10 per cent ammonium thiocyanate solution. Any red color should not be deeper than is produced by 0.05 mg. of iron under the same conditions.

PHENOLPHTHALEIN

REQUIREMENTS

Nonvolatile Matter—Not more than 0.050 per cent.
Insoluble in Alcohol—To pass test.
Solution in Sodium Hydroxide—To pass test.
Sensitiveness—To pass test.
Melting Point—Not below 258° C.

TESTS

Nonvolatile Matter—Ignite 2 grams and weigh. The residue should not weigh more than 0.0010 gram.

Insoluble in Alcohol—Dissolve 1 gram in 15 cc. of alcohol. The solution should be clear, with no insoluble residue.

Solution in Sodium Hydroxide—One gram should dissolve completely in a mixture of 90 cc. of water and 10 cc. of *N* sodium hydroxide.

Sensitiveness—Dissolve 0.1 gram in 10 cc. of neutral alcohol. Add 0.10 cc. of this solution to 200 cc. of carbon dioxide-free water, and add 0.05 cc. of 0.1 *N* sodium hydroxide. The solution should show a pink color when compared with an equal volume of water.

Melting Point—Determine by the method described in the U. S. Pharmacopeia.

POTASSIUM NITRATE

REQUIREMENTS

Insoluble Matter—Not more than 0.005 per cent.
Neutrality—To pass test.
Chlorine, Total—Not more than 0.002 per cent.
Iodate, Nitrite—To pass test (limit about 0.0005 per cent IO_3 ; about 0.001 per cent NO_2).
Phosphate (PO_4)—Not more than 0.0005 per cent.
Sulfate (SO_4)—Not more than 0.003 per cent.
Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Not more than 0.010 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent lead).
Iron (Fe)—Not more than 0.0003 per cent.
Sodium (Na)—To pass test (limit about 0.02 per cent).

TESTS

Insoluble Matter—Dissolve 10 grams in 50 cc. of water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The residue should not weigh more than 0.0005 gram.

Neutrality—Dissolve 5 grams in 50 cc. of water free from carbon dioxide, and add 3 drops of phenolphthalein. No pink color should be produced, but on the addition of 1 drop of 0.1 *N* sodium hydroxide a pink color should be produced.

Chlorine, Total—Ignite 1 gram, at first gently and then for a few minutes at a low red heat. Cool, dissolve in 20 cc. of water, add 1 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.02 mg. of chloride ion under the same conditions.

Iodate, Nitrite—Dissolve 1 gram in 10 cc. of water, add 2 drops of 10 per cent potassium iodide solution, 1 cc. of chloroform, and 2 cc. of 36 per cent acetic acid. Shake gently for a few minutes. The chloroform should not acquire a pink or violet color.

Phosphate—Dissolve 5 grams in 50 cc. of water, add 10 cc. of nitric acid, and nearly neutralize with ammonium hydroxide. Add 50 cc. of ammonium molybdate solution, shake (at about

40° C.) for 5 minutes, and allow to stand one-half hour. Any precipitate formed should not be greater than is produced when a quantity of an alkali phosphate containing 0.025 mg. of phosphate (PO_4) is treated according to the above procedure.

Sulfate—Dissolve 12 grams in 20 cc. of water, add 25 cc. of hydrochloric acid, and evaporate to dryness. Treat the residue with 15 cc. of water and 15 cc. of hydrochloric acid, and again evaporate to dryness. Dissolve the residue in 75 cc. of water, add 1 cc. of *N* hydrochloric acid, heat to boiling, add 5 cc. of 10 per cent barium chloride solution, heat on the steam bath for 2 hours, and allow to stand overnight. If any precipitate is formed, filter, wash, ignite, and weigh. The weight of the barium sulfate should not be more than 0.0010 gram greater than the weight obtained in a blank test with the same quantity of reagents and including filtration.

Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Dissolve 10 grams in 75 cc. of water, add 5 cc. of 4 per cent ammonium oxalate solution, 2 cc. of 10 per cent ammonium phosphate solution, and 15 cc. of ammonium hydroxide. Stir well and allow to stand overnight. If any precipitate forms, filter, wash, ignite, and weigh. The weight of the ignited precipitate should not exceed 0.0010 gram.

Heavy Metals—Dissolve 2 grams in 20 cc. of water and add 10 cc. of hydrogen sulfide water. No brown color should be produced.

Iron—Add ammonium hydroxide to the solution tested for heavy metals until it is alkaline. Any greenish color should not be greater than is produced by 0.006 mg. of iron in an alkaline sulfide solution.

Sodium—A 10 per cent solution tested with a platinum wire in the flame should give no distinct yellow color to the flame.

SODIUM FLUORIDE

REQUIREMENTS

Insoluble Matter—Not more than 0.050 per cent.

Chloride (Cl)—Not more than 0.01 per cent.

Free Acid (HF)—Not more than 0.2 per cent.

Free Alkali (as Na_2CO_3)—Not more than 0.25 per cent.

Sodium Fluosilicate (Na_2SiF_6)—Not more than 0.35 per cent.

Sulfate (SO_4)—Not more than 0.03 per cent.

Sulfite (SO_3)—Not more than 0.005 per cent.

Heavy Metals (as Pb)—Not more than 0.003 per cent.

Iron (Fe)—To pass test (limit about 0.003 per cent).

TESTS

Insoluble Matter—Dissolve 2 grams in 100 cc. of warm water in a platinum dish and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash thoroughly with hot water, dry at 105° to 110° C., and weigh. The weight should not exceed 0.0010 gram.

Chloride—Dissolve 0.3 gram in 20 cc. of water. Add 0.2 gram of boric acid, 1 cc. of nitric acid, and 1 cc. of 0.1 *N* silver nitrate. Any turbidity produced should not be greater than is produced by 0.03 mg. of chloride ion in an equal volume of solution containing the quantities of reagents used in the test.

Free Acid—Dissolve 2 grams in 40 cc. of water in a platinum dish, add 10 cc. of a saturated solution of potassium nitrate, and cool the solution to 0° C. Add 3 drops of phenolphthalein indicator. If no pink color is produced, titrate with 0.1 *N* sodium hydroxide until the pink color persists for 15 seconds while the temperature of the solution is near 0° C. Not more than 2 cc. of 0.1 *N* sodium hydroxide should be required.

Free Alkali—If a pink color is produced on the addition of the phenolphthalein in the test for free acid, add 0.1 *N* acid, stirring the liquid only gently, until the pink color is discharged. Not more than 0.5 cc. of the acid should be required.

Sodium Fluosilicate—Boil the solution from the preceding test and titrate while hot with 0.1 *N* alkali until a permanent pink color is obtained. Not more than 1.5 cc. of 0.1 *N* sodium hydroxide should be required.

Sulfate—Evaporate 0.5 gram in a platinum dish four or five times with 10 cc. of hydrochloric acid, evaporating the last time to dryness. Take up the residue in 20 cc. of water and 1 cc. of 0.1 *N* hydrochloric acid and filter if necessary. Add to the filtrate 2 cc. of 10 per cent barium chloride solution. Any turbidity produced in 10 minutes should not be greater than is produced by 0.15 mg. of SO_4 in a control made with the quantities of reagents used in the test.

Sulfite—Dissolve 6 grams in 150 cc. of water, add 2 cc. of hydrochloric acid and a few drops of starch solution, and titrate immediately with 0.1 *N* iodine. It should require not more than 0.1 cc. to produce a blue color.

Heavy Metals—Treat 2 grams in a platinum crucible with 10 cc. of hydrochloric acid and evaporate to dryness. Repeat with another 10 cc. of acid. Warm the residue with a few drops

of hydrochloric acid and dissolve in 40 cc. of hot water. Exactly neutralize 20 cc. with ammonium hydroxide, add 1 cc. of 0.1 *N* hydrochloric acid, and saturate with hydrogen sulfide. Any color produced should not be greater than is produced by 0.03 mg. of lead in an equal volume of water containing the quantities of reagents used in the test.

Iron—To the remaining 20 cc. from the test for heavy metals add 2 cc. of hydrochloric acid, filter if necessary, and add 3 cc. of 10 per cent ammonium thiocyanate solution. Any red color produced should not be more than is produced in a control test made with the same quantities of reagents and containing 0.03 mg. of iron.

SODIUM NITRITE

REQUIREMENTS

Insoluble Matter—Not more than 0.010 per cent.

Assay—Not less than 97 per cent.

Chloride (Cl)—Not more than 0.01 per cent.

Sulfate (SO_4)—Not more than 0.020 per cent.

Calcium (Ca)—Not more than 0.010 per cent.

Heavy Metals (as Pb)—Not more than 0.002 per cent.

Iron (Fe)—Not more than 0.001 per cent.

Potassium (K)—Not more than 0.01 per cent.

TESTS

Insoluble Matter—Dissolve 10 grams in about 100 cc. of hot water and allow to stand on the steam bath for 1 hour, filter through asbestos in a Gooch crucible, wash thoroughly, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0010 gram.

Solution A—Dissolve 10 grams in water and make to a volume of 100 cc.

Assay—Dilute 10 cc. of Solution A to 100 cc. Mix 300 cc. of water and 5 cc. of sulfuric acid and, while the mixture is still warm, add 0.1 *N* permanganate solution until a faint pink color is produced which persists for 2 minutes. Add 40 cc. of 0.1 *N* permanganate solution and mix gently. Run in slowly and with constant agitation 10 cc. of the sodium nitrite solution from a pipet, holding the tip of the pipet well under the surface of the liquid. Add 15 cc. of 0.1 *N* ferrous ammonium sulfate, and after allowing the solution to stand for 5 minutes, titrate the excess with 0.1 *N* permanganate. Each cc. of the permanganate consumed corresponds to 0.003450 gram of NaNO_2 .

Chloride—To 10 cc. of Solution A add 10 cc. of water, and add slowly 2 cc. of glacial acetic acid. Warm gently until no more gas is evolved, cool, and dilute to 25 cc. Add 1 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate solution. Any turbidity produced should correspond to not more than 0.1 mg. of chloride.

Sulfate—To 10 cc. of Solution A add slowly 2 cc. of hydrochloric acid and evaporate to dryness on the steam bath. Treat the residue with 1 cc. of dilute hydrochloric acid (1 + 9) and dilute with water to 10 cc. Add 1 cc. of 10 per cent barium chloride solution. Any turbidity produced should not be greater than is produced by 0.2 mg. of SO_4 under the same conditions.

Calcium—To 10 cc. of Solution A add slowly 1 cc. of glacial acetic acid. Heat to expel oxides of nitrogen, cool, dilute to 10 cc., and add 2 cc. of 4 per cent ammonium oxalate solution. Any turbidity produced should not be greater than is produced by 0.1 mg. of calcium under the same conditions.

Heavy Metals—To 20 cc. of Solution A add slowly 3 cc. of hydrochloric acid and evaporate to dryness on the steam bath. Treat the residue with 1 cc. of *N* hydrochloric acid, dilute to 10 cc., and add 2 cc. of hydrogen sulfide water. Any darkening should not be greater than is produced by 0.04 mg. of lead under the same conditions.

Iron—To 20 cc. of Solution A add 5 cc. of hydrochloric acid and evaporate on a steam bath almost to dryness. Take up the residue in 2 cc. of hydrochloric acid and 15 cc. of water; filter if necessary, and add to the solution 3 cc. of 10 per cent ammonium thiocyanate solution. Any red color produced should not be greater than in a control test made with the same quantities of the reagent and containing 0.02 mg. of iron.

Potassium—Dissolve 2 grams in a mixture of 10 cc. of water and 5 cc. of hydrochloric acid, and evaporate to dryness on the steam bath, finally heating for 15 minutes to about 120° C. Dissolve the salt in 10 cc. of water, and add 10 cc. of sodium cobaltinitrite solution and 7 cc. of alcohol. Any turbidity should not be greater than that produced by a blank containing 10 cc. of water and 10 cc. of cobaltinitrite solution to which have been added 0.2 mg. of potassium and 7 cc. of alcohol. (The sodium cobaltinitrite solution is made by dissolving 25 grams of NaNO_2 in 50 cc. of water and adding 15 cc. of 6 *N* $\text{HC}_2\text{H}_3\text{O}_2$ and 2.5 grams of $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ or an equivalent amount of nitrate or chloride. The solution is allowed to stand overnight, filtered, and diluted to 100 cc.)

TOLUENE

REQUIREMENTS

Boiling Range—110° to 111° C.

Nonvolatile Matter—Not more than 0.001 per cent.

Substances Darkened by Sulfuric Acid—To pass test.

Sulfur Compounds (as S)—Not more than 0.003 per cent.

Water—To pass test.

TESTS

Boiling Range—When 100 cc. are distilled by the method described in the U. S. Pharmacopeia, not less than 95 cc. should distil within the temperature range indicated.

Nonvolatile Matter—Evaporate 115 cc. on the steam bath and dry at 105° to 110° C. for 30 minutes. The weight of the residue should not be more than 0.0010 gram.

Substances Darkened by Sulfuric Acid—Shake 15 cc. with 5 cc. of sulfuric acid for 15 to 20 seconds and allow to stand 15 minutes. The toluene layer should be colorless and the color of the acid should not exceed that of a mixture of 2 volumes of water and 1 volume of a color standard containing 5 grams of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 40 grams of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and 20 cc. of hydrochloric acid in a liter.

Sulfur Compounds—Place 30 cc. of approximately 0.5 N alcoholic potassium hydroxide in an Erlenmeyer flask, add 6 cc. of the sample, and boil the mixture gently for 30 minutes under a reflux condenser. Detach the condenser, dilute with 50 cc. of water, and heat on the steam bath until the toluene and alcohol are evaporated. Add 40 cc. of saturated bromine water and heat for 15 minutes longer. Transfer the solution to a beaker, neutralize with dilute hydrochloric acid (1 + 4), add an excess of 1 cc. of the acid, and concentrate to about 50 cc. Filter if necessary, heat the filtrate to boiling, add 5 cc. of barium chloride solution, heat on the steam bath for 2 hours, and allow to stand overnight. If a precipitate is formed, filter, wash, and ignite. A blank should be run with the quantities of reagents used in the test and including filtration and ignition. The difference between the weights of ignited precipitates for the sample and for the blank should not be more than 0.0012 gram.

Water—Cool in crushed ice with the sample protected from moisture in the air. No cloudiness should be observed. Special care must be taken in handling the sample before as well as during this test to make sure that moisture has not been absorbed from the air.

XYLENE

REQUIREMENTS

Boiling Range—137° to 140° C.

Nonvolatile Matter—Not more than 0.002 per cent.

Substances Darkened by Sulfuric Acid—To pass test.

Sulfur Compounds (as S)—Not more than 0.003 per cent.

Water—To pass test.

TESTS

Boiling Range—When 100 cc. are distilled by the method described in the U. S. Pharmacopeia, not less than 95 cc. should distil within the temperature range indicated.

Nonvolatile Matter—Evaporate 115 cc. on the steam bath and dry at 105° to 110° C. for 30 minutes. The weight of the residue should not be more than 0.0020 gram.

Substances Darkened by Sulfuric Acid—Shake 15 cc. with 5 cc. of sulfuric acid for 15 to 20 seconds and allow to stand for 15 minutes. The xylene layer should be colorless, and the color of the acid should not exceed that of a mixture of 1 volume of water and 3 volumes of a color standard containing 5 grams of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 40 grams of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and 20 cc. of hydrochloric acid in a liter.

Sulfur Compounds—Place 30 cc. of approximately 0.5 N alcoholic potassium hydroxide in an Erlenmeyer flask, add 6 cc. of the sample, and boil the mixture gently for 30 minutes under a reflux condenser. Detach the condenser, dilute with 50 cc. of water, and heat on the steam bath until the xylene and alcohol are evaporated. Add 50 cc. of saturated bromine water and heat for 15 minutes longer. Transfer the solution to a beaker, neutralize with dilute hydrochloric acid (1 + 4), add an excess

of 1 cc. of the acid, and concentrate to about 50 cc. Filter if necessary, heat the filtrate to boiling, add 5 cc. of barium chloride solution, heat on the steam bath for 2 hours, and allow to stand overnight. If a precipitate is formed, filter, wash, and ignite. A blank should be run with the quantities of reagents used in the test and including filtration and ignition. The difference between the weights of ignited precipitates for the sample and for the blank should not be more than 0.0012 gram.

Water—Cool in crushed ice with the sample protected from moisture in the air. No cloudiness should be observed. Special care must be taken in handling the sample before as well as during this test to make sure that moisture has not been adsorbed from the air.

CORRECTIONS FOR PUBLISHED SPECIFICATIONS

Replace or modify requirements and tests previously printed as indicated below:

ACID MOLYBDIC ANHYDRIDE (4)

REQUIREMENT

Sulfate (SO_4)—Not more than 0.020 per cent.

TEST

Sulfate—Boil 1 gram with a mixture of 10 cc. of water and 5 cc. of nitric acid for 5 minutes. Cool thoroughly, dilute to 50 cc., mix well, and filter. Evaporate 10 cc. of the filtrate to dryness on the steam bath, warm the residue with 3 drops of hydrochloric acid and 10 cc. of water, filter if necessary, wash, make the filtrate to 50 cc., and add 1 cc. of 10 per cent barium chloride solution. Any turbidity should not be greater than is produced by 0.04 mg. of sulfate ion in the same volume of solution containing the quantities of acid and barium chloride used in the test.

CUPRIC OXIDE, POWDERED AND GRANULAR (6)

REQUIREMENT

Chloride (Cl)—Not more than 0.005 per cent.

TEST

Chloride—Make comparison with 0.05 mg. of chloride ion.

POTASSIUM IODIDE (3)

TEST

Heavy Metals—Third sentence should begin "Add 1 cc. of 0.1 N hydrochloric acid. . . ." Run a blank involving the use of the quantities of sulfuric and hydrochloric acids and ammonium hydroxide used in the test.

SODIUM BICARBONATE (2)

REQUIREMENT

Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Not more than 0.020 per cent.

TEST

Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Use corrected test (8).

SPECIFICATIONS PREVIOUSLY PUBLISHED

- (1) Committee on Analytical Reagents, IND. ENG. CHEM., 17, 756 (1925).
- (2) *Ibid.*, 18, 636, 759 (1926).
- (3) *Ibid.*, 19, 645 (1927).
- (4) *Ibid.*, 19, 1369 (1927).
- (5) *Ibid.*, 20, 979 (1928).
- (6) *Ibid.*, Anal. Ed., 1, 171 (1929).
- (7) *Ibid.*, 2, 351 (1930).
- (8) *Ibid.*, 3, 221 (1931).
- (9) *Ibid.*, 4, 154 (1932).

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Determination of Gum in Gasoline

A High-Temperature Modification of Air Jet Method

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THE most serious trouble in an automobile engine from the use of gasoline which will leave a residue of gum on evaporation, is encountered on the heated portions of the intake system and particularly around the inlet valve where the deposition of gum may cause sticking and improper seating (1, 6, 8, 12, 14, 16). Voorhees and Eisinger (14), and Hunn, Fischer, and Blackwood (8) have shown that the gum content of the gasoline at the time the fuel enters the intake system is the only significant figure with respect to the content of gum formed in the engine, and that potential gum is of no importance in this regard.

By gum content of a gasoline is meant the nonvolatile residue which will remain on evaporation of the gasoline. To obtain values for the gum content which are significant, it appears desirable to conduct the determination under conditions in some way approximating engine conditions, which are rapid evaporation on heated surfaces and in a stream of warm air.

In addition, a suitable routine method should be rapid and should produce duplicable results. A method which seems to approximate some of these requirements is described in this paper. It is a high-temperature air jet method, which is essentially a modification of the Hunn, Fischer, and Blackwood air jet method (8), and includes certain desirable features of the Norris and Thole method (12) and of that used by Mardles and Moss (10).

HIGH-TEMPERATURE AIR JET METHOD

The apparatus required for this method for the determination of the gum content of gasoline, and the procedure found

A simple and rapid method for the determination of the gum content of gasoline has been devised to approximate in some regards the conditions which exist during the deposition of gum in the intake system of an automobile engine. The procedure is essentially a high-temperature modification of the conventional air jet method. A glass beaker containing the gasoline is held in a well in a constant-temperature bath vessel, containing a liquid boiling at about 200° C. Air flowing at the rate of one liter per second and heated in passing through a tube incorporated in the bath vessel is used to evaporate the gasoline and dry the residual gum. The time required to obtain a sample of gum of substantially constant weight from 50 ml. of gasoline is 20 to 25 minutes. Oxidation during the determination is not an important source of error, reproducible results are obtained, and difficulties from creeping have not been experienced. Comparative data by this and by other methods are given.

most satisfactory are described below and illustrated in Figure 1.

APPARATUS. The dish used is a Berzelius-type beaker of heat-resistant glass, without lip, of 100 ml. nominal capacity.

The design of the bath is shown in Figure 1. The bath, which contains 0.5 to 0.75 liter of ethylene glycol (b. p. 195° to 200° C.), is fitted with a reflux condenser at the top of which a drying tube containing calcium chloride is connected. The bath should preferably be insulated with asbestos paper, and an electric hot plate capable of keeping the bath liquid boiling actively is the preferred heating means. In the absence of a satisfactory hot plate the bath may be heated by a gas burner, in which case the apparatus should be placed in a hood with a good draught. An electric immersion heater would probably be satisfactory also.

Tetrahydronaphthalene (tetralin), b. p. 200° to 205° C.,

was used initially as bath liquid, but it was found after it had been in use for a considerable time that it had decomposed somewhat with the formation of tar. A more stable liquid is therefore advisable, and ethylene glycol appears to be more satisfactory in this respect than tetralin and is tentatively recommended as the bath liquid to be used. One disadvantage in the use of ethylene glycol is that it readily takes up water with a consequent lowering of the bath temperature. The drying tube connected to the condenser will prevent this to a great extent. Objectionable amounts of water can readily be removed by detaching the condenser and boiling the liquid for a very short time, or by means of suitable drying agents. Certain other liquids which boil near 200° C. might be preferable to those mentioned.

For the air supply, low-pressure air is passed through a cotton or glass wool filter and is delivered to the preheater inlet of the bath. A flowmeter or other metering device is provided. A flowmeter is indicated in the diagram, but is not drawn to scale.

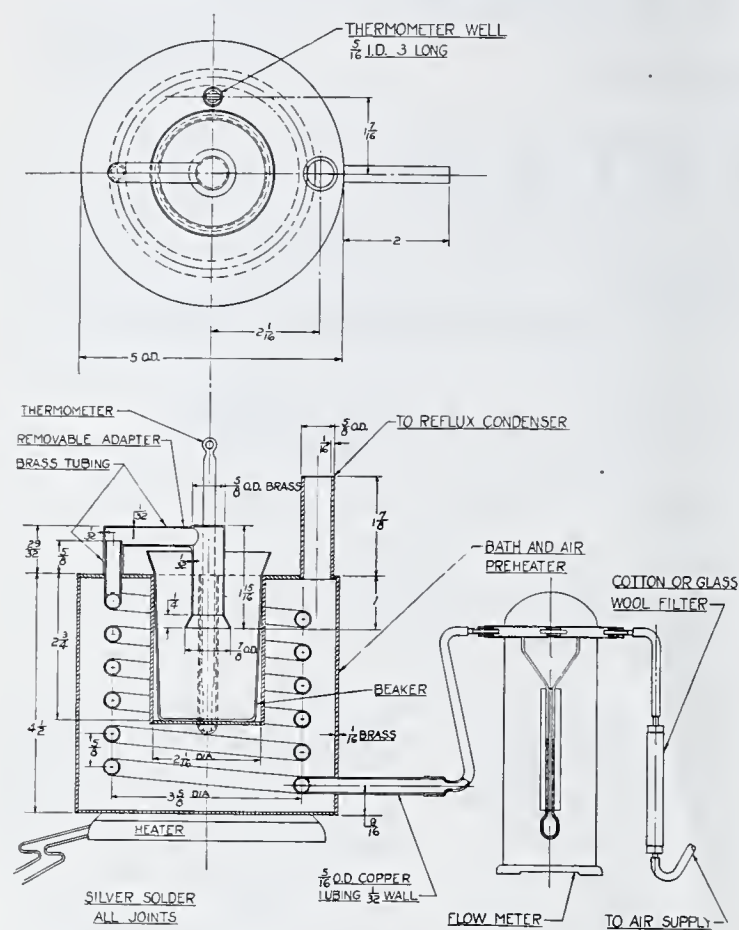


FIGURE 1. APPARATUS FOR DETERMINATION OF GUM CONTENT OF GASOLINE
(High-temperature air jet method)

PROCEDURE. Since the gum content of most commercial gasolines is very small, it is essential that care be taken in making the weighings, and it has been found that these must be made by tare to insure accuracy. A similar beaker which is subjected to exactly the same treatment as the test beaker (omitting the gasoline) is used as tare. In weighing such small amounts of gum as are frequently obtained, adsorbed moisture and temperature variations between the test beaker and the tare may seriously affect the results. To insure equilibrium in these respects, it has been found advisable to place the beakers, after they have cooled to room temperature, directly in the balance case, where they should remain one-half hour before the weighings are made.

The beaker is washed free of gum with a solution of acetone (or alcohol) and benzene, soaked for a few minutes in hot chromic acid solution, rinsed with water, dried with a lint-free cloth, and while held with crucible tongs, dried in the flame of a Bunsen burner. After cooling and weighing as described above, the beaker is placed in the well of the heated bath. The air rate is adjusted to one liter per second \pm 10 per cent. The metal adapter¹ is removed and 50 ml. of the test gasoline are poured into the beaker, after which the adapter is replaced on the air outlet so that the air stream is directed into the center of the beaker. After the gasoline has evaporated, which should require from 5 to 10 minutes, the beaker

¹ In a private communication, Graham Edgar, of the Ethyl Gasoline Research Laboratories, has informed us that with a similar apparatus trouble was experienced in initial experiments from copper oxide, apparently from the copper spiral, being deposited in the test beaker, but that an asbestos filter held in place with brass gauze was inserted in the adapter and the trouble was not experienced thereafter.

is left in place for an additional 15 minutes, the air supply being maintained. If the sample of gum obtained is very small, it is sometimes of advantage to evaporate a further 50-ml. sample in the same test beaker before drying the residue. The beaker is then allowed to cool and is weighed as described above. As is customary, the results are computed and expressed as milligrams of gum per 100 ml. of gasoline; this procedure is generally followed, but it is apparent from data in the literature, and it has been the authors' experience, that the gum value obtained on evaporating a 100-ml. sample is not twice that from a 50-ml. sample in the case of most gasolines. In this paper all gum values represent the actual weight of gum obtained.

COMPARISON OF GUM CONTENT VALUES BY VARIOUS METHODS

Comparative data on a number of gasolines have been obtained by the high-temperature air jet method and by certain other methods, which are briefly described here.

STEAM OVEN METHOD (4, 7, 11-15). The technic employed in these experiments resembled that of the Voorhees and Eisinger (14) modification of this method. The samples (50 ml.) of gasoline contained in glass evaporating dishes were held in an atmosphere of superheated steam at a temperature of 155° C. for 16 hours, in which time substantially constant weight has been reached. It has been the authors' experience with the steam oven method that, in general, at lower oven temperatures higher gum values are obtained.

AIR JET METHOD (2, 8, 9, 11). This method, designated in this paper as the conventional air jet method, was devised by Hunn, Fischer, and Blackwood (8). A 50-ml. sample of gasoline contained in an evaporating dish of heat-resistant glass (with lip; diameter of top 9 cm., and of base 4.5 cm.; depth 5 cm.) is held on a steam bath at 100° C., and the gasoline evaporated by means of a jet of unheated air flowing at the rate of about one liter per second; the evaporation requires about 15 minutes. The residue is then dried for one hour in an air oven at 150° C. It has been shown (8) and the observation confirmed in this laboratory that, if nitrogen or carbon dioxide be substituted for air during the evaporation of the gasoline, the results are in agreement with those found when using air; a fact which shows that at least during the evaporation of the gasoline atmospheric oxygen has been without effect. However, it has been the experience of Voorhees and Eisinger (14) with gum residues obtained by the steam oven test that drying in an air oven may sometimes permit the undried residue to take up oxygen and increase in weight.

100° C. DRIP METHOD. The conditions of the test are the same as for the conventional air jet method except that the gasoline is dripped from a separatory funnel into the evaporating dish at the rate of 3 to 4 ml. per minute. It has been found that the results obtained by this method, which was suggested by Fischer (5), do not differ greatly from those obtained by the conventional air jet method, and since supervision of the rate of dripping is necessary, no advantage is had over the latter method.

HOT DRIP METHOD. This method was devised prior to work on the high-temperature air jet method and, in view of certain data which are presented later, is described here, although it is not as convenient as the high-temperature air jet method. It was thought that there would be danger of very considerable oxidation occurring in an air jet method at upwards of 200° C., and so it was considered advisable to make preliminary experiments with a high-temperature drip method, in which each drop of gasoline evaporates in a very short time. The separatory funnel, as used in the 100° C. drip method, was found to be unsatisfactory under the conditions of this test, and the device which was utilized was the all-glass combined dripper and air-lead shown in Figure 2, the gasoline flowing from the reservoir through a capillary tube and being delivered at the rate of about 5 ml. per minute to the beaker, where the gum is deposited. Hot air is introduced simultaneously through the larger tube which surrounds the capillary at the rate of about one liter per second. The bath vessel shown in Figure 1 was also used here. With the device used, splashing of the dripping gasoline and creeping of the gummy deposit up the sides of the beaker were avoided and a fairly regular flow of gasoline was obtained, there being not more than one ml. of unevaporated gasoline in the beaker at any one time. Under these conditions, the evaporation of a 50-ml. sample of gasoline required about 10 minutes.

As in the high-temperature air jet method, the residue was dried in the hot air stream for 15 minutes. Since it was found that the values obtained with the hot drip method did not differ appreciably from those with the high-temperature air jet method, and since the latter method is simpler, it has been given the preference.

MODIFIED AIR JET METHOD. Data have also been obtained by a modified air jet method in which the bath vessel resembled that shown in Figure 1, but with a well designed to hold an evaporating dish of the type used in the conventional air jet method. The temperature on the bottom center of the dish directly below the adapter outlet was 175° C., when using tetralin as the bath liquid and with an air flow of one liter per second. Because of the shape it was not possible to dry the gum satisfactorily by means of the hot air jet, so the samples were dried for one hour in an air oven at 150° C.

In Table I data are given on six samples of gasoline which have been examined for gum content by the various methods described above. In the high-temperature air jet and the hot drip methods the bath liquid was tetralin, boiling at about 200° C. Samples A and E were found to be increasing rapidly in gum content, and to obtain comparative results, redetermination by certain methods was necessary. In general the values obtained in the high-temperature air jet method are near those of the hot drip and steam oven methods, and are about one-half those obtained by the conventional air jet and the 100° C. drip methods, and those of the modified air jet method are intermediate in value.

TABLE I. COMPARISON OF GUM-CONTENT VALUES BY VARIOUS METHODS

(Results expressed as mg. of gum per 50 ml. of gasoline evaporated)

GASOLINE	HIGH-TEMP. AIR JET, 190° C.	HOT DRIP, 190° C.	STEAM OVEN, 155° C.	CONV. AIR JET 100° C.- EVAPN., 150° C.- DRYING	100° C. DRIP, 100° C.- EVAPN., 150° C.- DRYING	MODIFIED AIR JET, 175° C.- EVAPN., 150° C.- DRYING
	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
A (original)		118 127 137	135 138	313 316	319 323	153 162
A (later)	174 172.5		193	474		
B	2.5 2.4	2.9 3.0	2.9 2.8	4.8 4.6	5.2 5.1	3.5 2.7
C	5.3 5.2	6.3 6.2	5.6 6.0	10.4 10.1	11.9 11.4	6.6 6.5
D	10.0 9.9 10.4 10.3	10.6 10.3	11.4 12.5	18.7 18.2	17.6 19.8	11.0
E	38.1 37.8	39.0	40.4 43.8 45.7	70 78 90 95 111	68 79 85 105	40.4 41.2
F	20.7 21.0 21.0	21.7 19.9	25.7 25.9		44.1	

Time in minutes

to obtain dry

sample of gum: 20-25

25-30

Several hrs.

70-80

70-80

70

EFFECT OF PROLONGING DRYING OF GUM

Littlejohn, Thomas, and Thompson (9) found that the time required for drying residues of gum obtained by air jet tests to substantially constant weight depended greatly on the temperature, and that the final gum value was also dependent, as would be expected with residues of a volatile nature, on the temperature of drying. Bridgeman and Aldrich (2) likewise found that there was a change in weight of the residue with time of heating and that at a drying temperature of 102° C. gum residues of the conventional air jet method required from 3 to 16 hours to reach approximately constant weight.

It has been found that the gum residues of the conventional air jet method are not dried to constant weight on heating in a 150° C. air oven for one hour, but the subsequent loss in

weight does not materially affect the results. This is also the case with the gum residues of the high-temperature air jet method, where the major part of the drying takes place in the specified 15-minute period, but a further small decrease in weight may result with certain types of gum on prolonged drying. The residue is dried to such an extent after 15 minutes in the hot air stream that no further decrease in weight occurs on subsequent drying in an air oven at 150° C. for a few hours. But if, on completion of the evaporation, the sample is dried to substantially constant weight, first in an air oven at 150° C., and then in the hot air stream at 200° C., it is found that these weights are not the same, but that a considerable decrease in weight has occurred as a result of the drying in the hot air stream. It also appears that as a result of the preliminary drying in the air oven the final weight attained, after a treatment such as that just outlined, is greater than had the drying been done in the hot air stream initially. This may be the result of oxidation occurring during the drying of the residue in the air oven. Data from nine experiments are given in Table II.

Various samples of gum obtained during the preparation of data for Table I by the conventional air jet, the modified air jet, and the 100° C. drip methods were dried further after the initial drying period of one hour in a 150° C. air oven, and were found to have decreased in weight by percentages ranging from zero to 17 after 45 hours at 150° C., and from 6.5 to 30 after 45 hours at 180° C. When a calculation was made on the basis of the total weight of gum of all samples so treated, it was found that the prolonged drying at 150° C. had brought about a decrease in weight of approximately 4 per cent, and at 180° C. of about 10 per cent.

Two such experiments with gum residues of the conventional air jet method in which the drying was done in an air oven at 150° C. are:

		Gram
Gum from gasoline sample A:		
Dried one hour		0.4740
Dried 16 hours further		0.4577
Decrease in weight		3.5%
Gum from gasoline sample E:		
Dried one hour		0.1110
Dried 16 hours further		0.1021
Decrease in weight		8%

EFFECT OF ATMOSPHERE

Yule and Wilson (17) point out that with a method of evaporation of the gasoline such as the conventional air jet method the atmospheric oxygen may cause considerable oxidation to take place during the test. Norris and Thole (12) find that under their conditions of test this effect may not be very great, the values obtained using nitrogen being

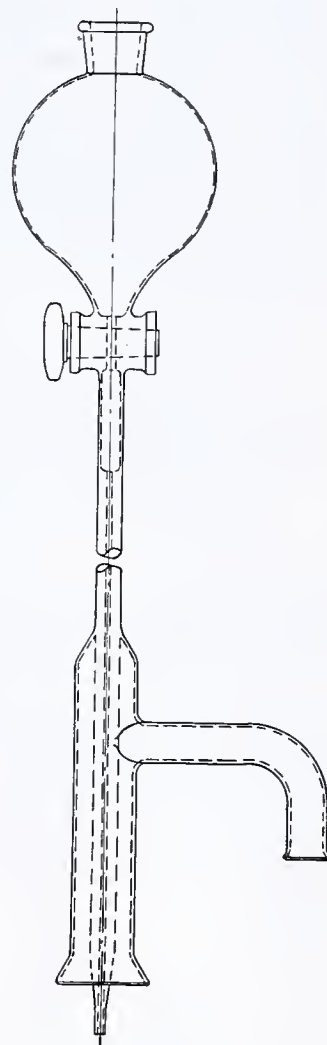


FIGURE 2. COMBINED DRIP-PER AND AIR-TUBE ADAPTER, ALL GLASS (Hot drip method)

only 10 to 15 per cent less than when using air. The process of gum deposition by the hot drip method is not unlike that by the Norris and Thole method, and it is probable that there would be agreement between gum values obtained by these two methods. In Table III are given values on five samples of gasoline, obtained with air, nitrogen, and carbon dioxide as the gases used for the evaporation of the gasoline and the drying of the gum. Samples H, P, and I are very gummy and would scarcely be encountered commercially. The agreement shown between the hot drip and the high-temperature air jet methods under the same conditions is excellent, and the variation between values obtained using air and the other two gases is not great and indicates that the simple method of evaporating the gasoline and drying the residual gum with a strong jet of heated air is satisfactory, in the case of the gasolines examined, in avoiding very considerable oxidation from atmospheric oxygen.

TABLE II. EFFECT OF PROLONGING DRYING OF GUM (High-temperature air jet method)				
GASOLINE	TOTAL TIME OF DRYING AT 190° C. Min.	AIR RATE Liters/sec.	GUM PER 50 ML. OF GASOLINE Mg.	DECREASE FROM INITIAL %
D	16	0.3 to 0.5	10.4	
	32	0.3 to 0.5	10.4	
	52	0.3 to 0.5	10.3	1
	67	0.3 to 0.5	10.1	3
	88	0.3 to 0.5	10.1	3
	111	1.3 to 1.6	10.1	3
D	15	1.4 to 1.7	10.3	
	30	1.4 to 1.7	10.3	
	45	1.4 to 1.7	10.0	3
	64	1.4 to 1.7	9.8	5
	79	1.0 to 1.2	9.8	5
	101	1.3 to 1.6	9.8	5
D	70 (air oven, 150° C.)		13.7	
	130 (total)		13.5	(1.5)
	19	0.5	11.6	(15), 0
	34	0.5	11.2	
	49	1.0 to 1.2	11.3	(17.5), 2.5
	65	1.0 to 1.2	11.3	(17.5), 2.5
D	15	1	9.9	
	30	1	9.4	5
	45	1	9.3	6
A	15	1	174.1	
	30	1	172.9	0.7
	60 (air oven, 150° C.)		172.9	0.7
	45	1	172.8	0.7
A	15	1	172.3	
	60 (air oven, 150° C.)		172.2	
	30	1	171.3	0.6
C	15	1	5.2	
	30	1	5.1	
	45	1	5.2	
C	15	1	5.3	
	60 (air oven, 150° C.)		5.4	
	30	1	5.3	
E	15	1	37.8	
	30	1	36.4	4
	45	1	36.2	4.5

VARIATION IN GUM CONTENT WITH AIR RATE

In determining the gum content of gasoline by the high-temperature air jet method it is essential that the air flow be sufficiently rapid to remove the gasoline and dry the gum effectively in a short time, in order to minimize tendencies towards excessive oxidation and abnormal polymerization of gum-forming constituents of the gasoline. This is apparent from data given on sample I (Table III), and further corroborative data are shown in Figure 3. The values were obtained on the same sample of gasoline, but at two different temperatures; this was sample H, a composite of gummy gasolines of high gum content, on which data are also given in Table III at an experimental temperature intermediate between the temperatures here. For the values shown on curve 1, the bath liquid was a technical grade of ethylene glycol, and for those on curve 2 tetralin, the temperature of the hot air jet being about 8° C. higher in the latter case. It is

seen from Figure 3 that this variation in temperature has but a very small effect on the gum value in comparison with that resulting from variation in air rate. It also appears that as the air rate is raised, the tendency towards decrease in the gum value is approaching a limit which may be near that which would be obtained when using an inert gas jet. It is seen from the curves that the variation in gum values with air rate is not great when the air rate is near one liter per second, and since in using somewhat greater rates of air flow there are difficulties encountered, such as entrainment of droplets of the gasoline in the very strong air stream, the air rate was set as one liter per second in the high-temperature air jet method.

TABLE III. EFFECT OF SUBSTITUTING NITROGEN AND CARBON DIOXIDE FOR AIR DURING EVAPORATION AND DRYING PERIODS IN HIGH-TEMPERATURE METHODS

GASOLINE	GAS	RATE OF FLOW Liters/sec.	GUM PER 50 ML. BY HIGH- TEMPERATURE AIR JET METHOD	GUM PER 50 ML. BY HOT DRIP METHOD
			Mg.	Mg.
G	Air	1	9.6	
	Nitrogen	1	9.1	
H	Air	0.9	35	34
	Nitrogen	0.9	30	30.5
	Carbon dioxide	0.9	29.5	30
I	Air	1	198, 201	
	Air	0.4 to 0.5	240	
	Air	1.25	192	
	Nitrogen	1	168, 168.5	
	Nitrogen ^a	1	186.5	
	Carbon dioxide	1	167	
	Carbon dioxide ^b	1	205	
P	Air	1	47.7	
	Nitrogen	1	44.7	
	Carbon dioxide	1	45.4	
P-1	Air	1	16.1	
	Nitrogen	1	14.9	
	Carbon dioxide	1	15.6	

^a Gasoline evaporated with nitrogen and gum dried with air, same rate of flow in both cases.
^b Gasoline evaporated with carbon dioxide, dried in carbon dioxide atmosphere at very small gas flow (gum, 223 mg.), then dried with air flowing at 1 liter per second for 15 minutes (gum, 205 mg.).

TEMPERATURES RECORDED DURING AN EXPERIMENT

The temperatures, as recorded by a thermometer touching the bottom center of the beaker below the adapter outlet, both during the evaporation of a sample and the drying of the residual gum by the high-temperature air jet method, are given in Table IV. In this experiment the bath liquid was tetralin (b. p. 202° C.), and the air rate was one liter per second. It is seen that the temperature of the gasoline is quite moderate during most of the short time required for evaporation, a fact which may account for the good correlation found between the hot drip and the high-temperature air jet methods.

TABLE IV. TEMPERATURES RECORDED DURING HIGH-TEMPERATURE AIR JET GUM DETERMINATION

(By thermometer touching bottom center of beaker)			
TIME ^a Min.	TEMP. ° C.	TIME ^a Min.	TEMP. ° C.
0	43	8	188
1	62	8.5	190
2	78	9	192.5
3	96	10	193.5
4	112	11	193.5
5	129	18	194
6	150	22	194
7	167		
7.3	Evaporation over		

^a From start of evaporation.

The temperature distribution is very even at points where gum may be deposited in the beaker used in the high-temperature air jet method. The temperature was explored by means of a thermocouple under the variety of conditions recorded in Table V. The thermometer temperature with different rates

of flow is also given. The bath liquid was ethylene glycol with a boiling point of 195.5° C.

TABLE V. TEMPERATURES MEASURED BY THERMOCOUPLE HELD IN VARIOUS POSITIONS IN BEAKER

(High-temperature air jet method; bath liquid, ethylene glycol)					
Air flow, liters/sec.	0.4	0.5	0.75	1.0	1.2
	° C.	° C.	° C.	° C.	° C.
Positions of thermocouple					
1. At levels where gum may be deposited:					
Touching bottom center	182.5	186	184.5	187.5	188
Touching bottom side	185	183	186.5	187.5	188
In air jet below outlet	179	182	181.5	186	186
At adapter outlet level					
halfway to beaker wall	178.5		184	184.5	186
Touching side 1/3 way up	182.5	186	186	187	187
Same half way up	182.5		182	185.5	185.5
Same 2/3 way up					184.5
Av.	181.7	184.2	184.1	186.3	186.4
2. At levels where gum is not deposited:					
Touching side at well top	152				172
Same opposite side	160			160	160
Touching side 3/4 way up				175	
Thermometer resting on bottom center	179	182	183	185.5	187

VOLATILITY OF GUM-FORMING CONSTITUENTS

Brookes (3) has pointed out the complex nature of the gum-forming constituents of gasoline, and Yule and Wilson (17) have shown that certain of these can be prevented from taking part in the deposition of the gum if the evaporation is carried out with rapidity and at a sufficiently high temperature. Under the conditions of evaporation existing in the intake system of an engine, and also in the high-temperature air jet method, the observations of Yule and Wilson should also be true. Certain data, presented later, obtained with the high-temperature air jet method on the effect of dilution on gum content values made it advisable to obtain further evidence as to the volatility of gum-forming constituents.

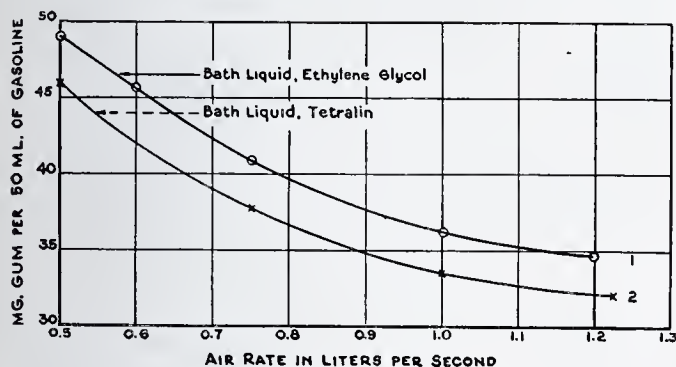


FIGURE 3. VARIATION IN VALUES WITH AIR RATE (High-temperature air jet method)

These experiments show that the gum-forming constituents are not completely removed from a gasoline containing gum by relatively slow distillation, and that in such a distillation the residual gum may increase very considerably.

STEAM DISTILLATIONS. In one experiment where 200 ml. of distilled water and 110 ml. of sample H, which had increased somewhat in gum content from the value previously obtained, were distilled until about 5 ml. of water remained in the flask, it was found that the total gasoline in the distillate had a gum content of 3.6 mg. by the high-temperature air jet method. The residue in the flask was taken up in acetone and the gum determination showed 140 mg. In another similar experiment with sample H, it was found that when only one-half the gasoline was distilled off, the gum content of the total gasoline distilled was 1.2 mg.

It was thought that atmospheric oxygen might have been responsible for part of the gum formation in the above experiments, and so an experiment was made in which the distillation took place in a nitrogen atmosphere and the gum determinations were made with a high-temperature nitrogen jet. Distillation was made of 100 ml. of sample H and 200 ml. of distilled water until about 5 ml. of water remained in the flask. The residue

of gum from the total gasoline distilled was 2.7 mg. and that in the flask was 142 mg., indicating that atmospheric oxygen had apparently been without appreciable influence in the former experiments. However, this does not exclude the possibility of oxidation occurring in these cases from compounds containing oxygen, or from atmospheric oxygen dissolved in the gasoline.

The gum content of sample H by the high-temperature air jet method, at the time these experiments were made, was 38.1 mg. per 50 ml. The very considerable increase in total gum in the sample over this value may be due to acceleration of

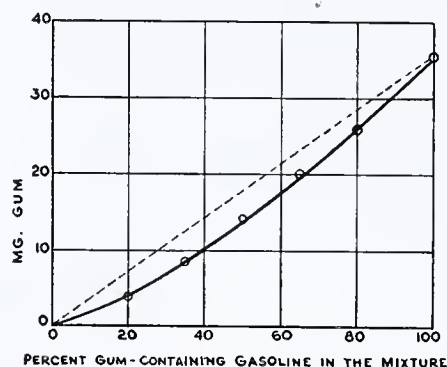


FIGURE 4. GUM DETERMINATIONS BY HIGH-TEMPERATURE AIR JET METHOD ON MIXTURES OF GUM-CONTAINING GASOLINE WITH GUM-FREE STRAIGHT-RUN GASOLINE (TOTAL VOLUME, 50 ML.)

formation of gum from constituents of the gasoline by heating; and to chemical reaction of certain gum-forming constituents with the steam may perhaps be ascribed the small increase in total gum formation here as compared with that in the experiments described below.

OTHER DISTILLATIONS. In these distillations an undiluted sample of gasoline H and 50 per cent mixtures of gasoline H with xylene and with petroleum ether were distilled until the residue in the flask amounted to about 3 ml. The volume of the sample was 50 ml. in each case. In the case of the petroleum ether mixture, there was a loss of 2 ml. during the distillation. The values were obtained by the high-temperature air jet method.

	DISTILLATE Mg.	FLASK RESIDUE Mg.
Undiluted sample H	2.3	102
Sample H and xylene	0.2	45.5
Sample H and petroleum ether	0.7	47.5

These experiments confirm the observations of Yule and Wilson that some gum-forming constituents can be distilled with the gasoline. These distillations were made at a slow rate; Yule and Wilson found, under a condition of flash evaporation at a temperature near 200° C., that 90 per cent of the peroxide content of a gasoline could be distilled without taking part in gum formation. Such data indicate that gum which will separate on evaporation of gasoline is greatly dependent on the conditions existing during the process of evaporation. The great increase in gum content of sample H, which results from holding the gasoline at an elevated temperature for a relatively short time, indicates the advantage of having a rapid and efficient method of evaporating the gasoline and drying the residual gum, if it is desired to approximate the conditions of rapid evaporation on heated surfaces and in a stream of warm air, which presumably exist in an engine.

EFFECT OF DILUTION ON GUM-CONTENT VALUES

Some workers (2, 11) have intimated that a possible criterion for accuracy in gum determination methods is that the value obtained for a 50 per cent mixture of a gummy gasoline with a gum-free gasoline should be one-half that for the undiluted gummy gasoline sample. If gum were a pure substance dissolved in the gasoline this might be expected to be the case, but the gum ordinarily obtained on the evaporation of gasoline does not meet this requirement. To cite only one exception, gum when once separated by evaporation can only

rarely be dissolved in the parent gasoline, whether deposited in laboratory tests or under the conditions existing in an engine. It has been pointed out above that a certain amount of the gum-forming material present in the gasoline can be distilled even in a relatively slow process of distillation. The amount of residual gum obtained on evaporation should be expected to be greater when dilution of the gasoline is made with an equal volume of liquid of low boiling point than when the diluent is of high boiling point. In the former case the amount of gum ordinarily deposited from gasolines containing gum-forming constituents should therefore be less than one-half the value obtained for the undiluted sample.

TABLE VI. GUM CONTENT OF 50 PER CENT MIXTURES OF GUM-CONTAINING GASOLINES WITH VARIOUS GUM-FREE DILUENTS

(High-temperature air jet method) ^a		(1) GUM FROM 50 ML. OF UN- DILUTED SAMPLE	(2) GUM FROM 50 ML. OF DILUTED SAMPLE	RATIO OF (2) TO (1) %
GASOLINE	DILUENT (B. P., ° C.)	Mg.	Mg.	
H	Mineral Seal oil (260–320)	38.1	22.6	59
H	Xylene (140)	38.1	23.4	61
H	"Cellosolve acetate" (140–160)	38.1	17.3	45
H	n-Heptane (98)	38.1	15.2	40
H	Commercial cracked gasoline (I. B. P. 30, E. P. 200)	38.1	15.1	39.6
H	Petroleum ether	38.1	15.0	39.4
H	Straight-run gasoline (I. B. P. 30, E. P. 175)	38.1	14.7	38.6
L	Straight-run gasoline (I. B. P. 30, E. P. 175)	8.4	3.1	37
J	Straight-run gasoline (I. B. P. 30, E. P. 175)	18.3	7.2	39
K	Straight-run gasoline (I. B. P. 30, E. P. 175)	25.4	9.6	38
N	Straight-run gasoline (I. B. P. 30, E. P. 175)	41.7	16.9	41
Q	Straight-run gasoline (I. B. P. 30, E. P. 175)	5.0	2.5	50
R	Straight-run gasoline (I. B. P. 30, E. P. 175)	15.5	7.1	46

^a All gums were of resinous type, except in case of gasoline Q where gum was of oily type, and in case of gasoline R where residue was partly oily, partly resinous, and partly composed of water-soluble solid.

In Table VI are given the results of a number of experiments on 50 per cent mixtures of gummy gasolines with various diluents, and in Figure 4 are shown the gum-content values obtained for different concentrations of a gummy gasoline with a gum-free straight-run gasoline. Gum determinations were made on all liquids used as diluents in the pure state, and of these only Mineral Seal oil left a residue of gum; in this case the value given in Table VI has been corrected. The results point to the presence of gum-forming constituents in most of the gummy gasolines used. Only in the case of gasoline Q could the deposited gum be completely redissolved in the original gasoline. It is also evident, from the results with gasoline H, that when the diluent is of high boiling point the gum-content value found approaches one-half the value for the undiluted sample more nearly than is the case when the diluent is of low boiling point. In certain cases the value found is greater than one-half the value for the undiluted sample, and in the case of Mineral Seal oil this may be ascribed to a prolongation of the evaporation period, thereby enabling the gum-forming material to play its role more effectively than during the evaporation of the undiluted gasoline.

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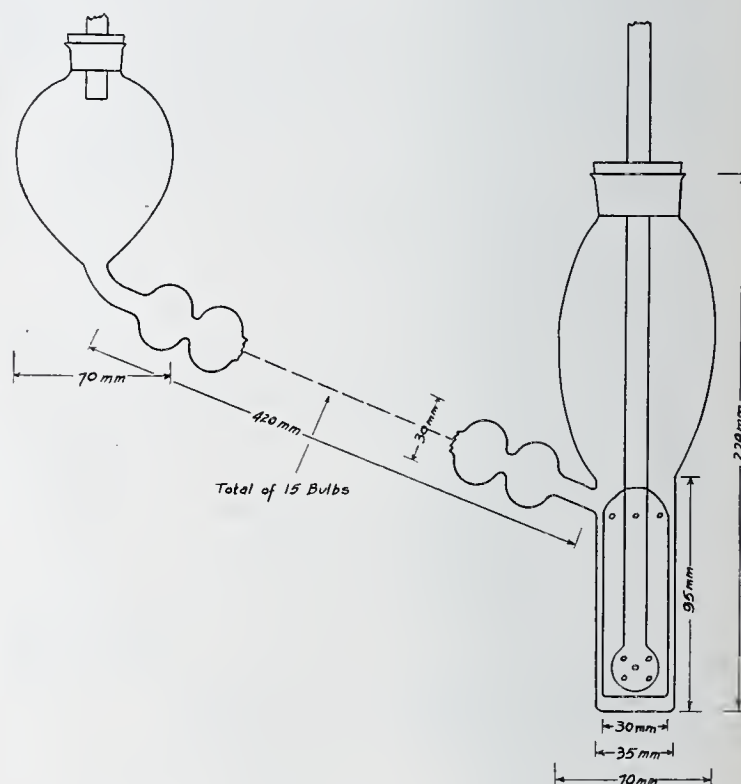
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RECEIVED May 25, 1932.

An Efficient Absorption Tube

E. F. DEGERING, Purdue University, Lafayette, Ind.

THE accompanying figure shows a combination of the Folin and Meyer absorption tubes. This type of tube has proved much more efficient as a gas scrubber than either the Folin or the Meyer tubes, and is especially useful as absorption apparatus where a rather rapid flow of a gas is being scrubbed by suitable liquid absorbents.



The dimensions given in the drawing are for a tube holding about 150 cc. of the absorbing liquid or solution. Tubes of proportionate size would satisfy the requirements for smaller or larger amounts of the absorbent.

If made of Pyrex glass and properly handled, tubes of this type are quite durable and very satisfactory in analytical procedures. These tubes were designed and made as a means of affording more accurate determination of carbon dioxide by the wet method where a rapid flow of the gases was required.

RECEIVED May 5, 1932. Tube designed and made in connection with a research problem at the University of Nebraska.

Determination of Carbon Dioxide in Gas Mixtures

A Potentiometric Method

P. W. WILSON, F. S. ORCUTT, AND W. H. PETERSON, University of Wisconsin, Madison, Wis.

THE need for a rapid, accurate method of estimating carbon dioxide is common to many branches of science. A large number of studies in both theoretical and applied chemistry demand simple methods for determining small percentages of carbon dioxide in air and other gaseous mixtures. It is not surprising that many ingenious devices have been developed in an effort to satisfy this need. The majority of the proposed methods can be classified into the following types: (1) those in which the $PV = K$ property of gases is utilized; (2) those in which the carbon dioxide in a known volume of gas is absorbed in alkali and subsequently measured by chemical or physical means. The first class includes those methods in which special apparatus is required—e. g., the Haldane, Van Slyke, or Warburg gas analysis apparatus. Methods of the second class are more frequently used because the apparatus is less expensive and the determination is simple. However, an accurate gas meter is often required, and this is not standard equipment in most laboratories.

A method that belongs to neither of these classes is available but because of certain technical difficulties, little work has been reported on it. This method depends upon the measurement of the equilibrium between the carbon dioxide in an atmosphere and a sodium bicarbonate solution of known concentration. The equilibrium is usually determined by estimating the hydrogen-ion activity or pH. If this is done by means of the hydrogen electrode, elaborate precautions must be maintained to avoid displacement of the equilibrium, hence the method becomes too tedious for routine analyses. Recourse to colorimetric methods, such as proposed by Haas (4), Higgins and Marriot (7), and McClendon (11), has proved of value, but this expedient has sacrificed accuracy to ease of operation. Since colorimetric standards can be read to less than 0.1 pH only with difficulty, the error involved in a determination may be considerable. The accuracy of this method has been increased by determining the pH potentiometrically with the glass electrode, and thus the qualities necessary for routine analyses—i. e., rapidity, simplicity, and ease of operation—have been preserved. The method as finally developed is accurate to 0.02 pH (one millivolt) which is the limit of accuracy of the potentiometer set-up in this laboratory. The only apparatus required is a vacuum-tube potentiometer, or any other devices suitable for measuring pH with the glass electrode. Since the glass electrode method for the determination of pH is gaining favor in biological and chemical laboratories, this method should be available to many without the expense of additional equipment.

A rapid, accurate method is described for measuring low percentages (0.03 to 7 per cent) of carbon dioxide in gas mixtures. It consists of bubbling the gas mixture through about 10 cc. of dilute sodium bicarbonate solution, then determining the pH of the solution with the glass electrode. From a calibration curve the $p\text{CO}_2$ can be readily ascertained. The theory upon which the method is based is discussed. For routine analyses a set-up is described which combines speed and ease of operation with a maximum error of 4 per cent. For a greater accuracy, certain refinements are indicated. The method can be modified for use with a pH colorimeter, if a suitable potentiometric set-up is not available.

THEORETICAL DATA

The principle of the method is based on the buffering effect of a salt of an acid when added to a solution of the acid; for example, in an aqueous solution of carbonic acid and sodium bicarbonate the pH will be a function of the activities of the bicarbonate ion and carbonic acid present. The latter depends on the partial pressure of the carbon dioxide in the atmosphere which is in equilibrium with the solution. If the activity of the bicarbonate ion is fixed, then the pH is a function solely of the partial pressure of the carbon dioxide that is in equilibrium with the sodium bicarbonate

solution. Since carbonic acid is only very slightly ionized in solution, the effective concentration (or activity) of the bicarbonate ion is sensibly that of the sodium bicarbonate present in the solution. It follows that if a dilute solution of sodium bicarbonate of known concentration is brought to equilibrium with an atmosphere containing carbon dioxide, the final pH of the solution measures the $p\text{CO}_2$ in the atmosphere and is independent of the volume of gas passed through or the volume of sodium bicarbonate used.

Because of the importance of this sodium bicarbonate-carbonic acid equilibrium in physiological chemistry, intensive studies of the reaction have been made by a large number of investigators. Hasselbach (5) studied this equilibrium and derived the equation

$$\text{pH} = \text{p}K + \log \delta + \log \frac{(\text{HCO}_3^-)}{(\text{CO}_2)} \quad (1)$$

where $\text{p}K$ represents the negative log of the first dissociation constant of carbonic acid, and δ the degree of dissociation of sodium bicarbonate in the solution used.¹ Warburg (13) discussed the equation and the data of Hasselbach in light of the new theory of complete dissociation of strong electrolytes, and pointed out that Hasselbach's treatment was merely a first approximation, since concentrations rather than activities were employed. Warburg then developed the corrected mathematical relations for use under various assumptions and conditions. He showed that the bicarbonate ion due to the dissociation of the carbonic acid can be neglected if a concentration of sodium bicarbonate is used such that

$$\frac{cH}{cM} < 0.01$$

where cH is the concentration of hydrogen ions and cM is the concentration of the sodium bicarbonate. Also, he

¹ If δ is the activity coefficient of sodium bicarbonate, this equation is correct and is independent of any theory (see Equation 2).

demonstrated that if the measured pH was less than 8.0, the error arising through neglect of the second dissociation constant of carbonic acid is negligible. Hastings and Sendroy (6) studied the application of the Debye-Hückel theory of electrolytic dissociation to the sodium bicarbonate-

extended this work and verified the value of pK_{∞} . These workers also discuss the variation of the value of this constant with temperature. The value of $\Delta pK_{\infty}/\Delta T$ varied from 0.005, based on e. m. f. measurement, to 0.0069 based on Thomsen's colorimetric determinations; the best agreement was among the e. m. f. measurements.

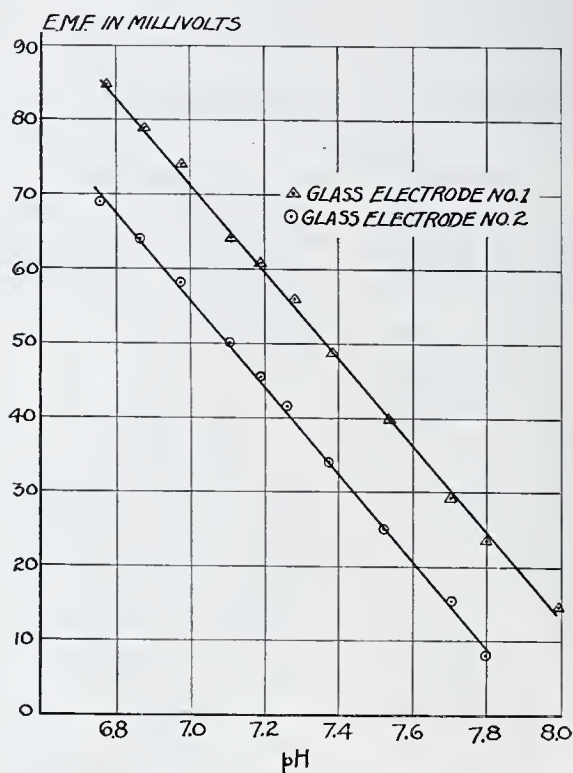


FIGURE 1. CHANGE OF E. M. F. WITH pH USING GLASS ELECTRODES

carbonic acid system in the presence and absence of other ions—e. g., sodium chloride. The theoretical equation applicable to the system that was derived by these investigators is:

$$pK_1 + \log \gamma_1 = \text{pH} - \log (\text{NaHCO}_3) + \log p\text{CO}_2 + \log \frac{\alpha_{\text{CO}_2}}{760 \times 22.4} \quad (2)$$

where $pK_1 = -\log K_1$
 K_1 = apparent first dissociation constant of carbonic acid
 γ_1 = activity coefficient of sodium bicarbonate in concentration used
 (NaHCO_3) = molal concentration of NaHCO_3
 $p\text{CO}_2$ = partial pressure of CO_2
 α_{CO_2} = solubility coefficient of carbon dioxide in water at temperature used

If $pK_1 + \log \gamma_1$ is designated by pK_1' , this latter will be a constant for a given concentration of sodium bicarbonate, and according to the Debye-Hückel theory should vary with the concentration in dilute solutions according to the following equation:

$$pK_1' = pK_{\infty}' - 0.5 \sqrt{\mu} \quad (3)$$

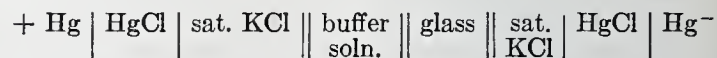
where pK_{∞}' = value of pK_1' at infinite dilution
 μ = ionic strength = $1/2 \sum c_i v_i^2$
 v_i = valence of ions
 c_i = molal concentration of ions

Using very exact experimental technic, Hastings and Sendroy determined the value of pK_1' over a range of concentrations of sodium bicarbonate extending from 0.01 to 0.03 normal with and without added sodium chloride, so that the ionic strength varied from 0.01 to 0.18. Their results closely followed the equation predicted by the theory and gave a value of pK_{∞} of 6.33 at 38° C. Stadie and Hawes (12)

EXPERIMENTAL PROCEDURE

DETERMINATION OF pH. The method was developed to measure the carbon dioxide in air supplied to plants grown in atmospheres containing 0.1 to 1 per cent of this gas. It was necessary to use 0.001 *N* solutions of sodium bicarbonate for the lower concentrations of carbon dioxide and 0.01 *N* for the higher. An attempt was made to use the quinhydrone electrode to measure the pH, but this proved unsatisfactory because of the drifting of the e. m. f. Glass electrodes were next tried and proved very satisfactory. The vacuum-tube potentiometer used to measure the e. m. f. was a modification of the type described by Allyn and Baldwin (1). This set-up employs a UX-199 vacuum tube, the grid bias of which is adjusted as closely as possible to the value at which there is zero grid current (floating grid potential). The actual grid current obtained, although varying considerably, was never greater than 10^{-12} amperes. This potentiometer is simple in construction, inexpensive, and gives reproducible results with a minimum of care. It is sensitive to one millivolt which was sufficiently accurate for these purposes. Glass electrodes as described by MacInnes and Dole (8, 9) were first tried, but because of the necessity for frequent handling, transportation, etc., these were found to be too fragile. The electrode finally adopted was made by sealing about 3 cm. of 6-mm. Corning 015 glass (9) to 20 cm. of ordinary soft glass, then blowing a fairly thin bulb about 10 mm. in diameter on the special glass end. The thickness of this bulb is limited to the sensitivity of the potentiometer employed and can best be determined by trial. The desiderata of these electrodes are that they should be sturdy enough to withstand considerable shock in handling and yet give a constant, reproducible potential when used to measure the pH of a standard buffer solution. As the bulbs increase in thickness, the potentials become less reproducible, because of changes in body capacity, leakage currents in the circuit, variations in grid current, etc. With a little practice the desirable thickness is readily ascertained; an actual test is the final criterion as to whether or not a suitable bulb has been blown. Measurements on a typical bulb indicated that the glass membrane was about 50 microns in thickness; the resistance of these bulbs is of the order of 200 to 250 megohms.

After a suitable bulb has been blown, the electrode is filled with saturated potassium chloride solution and aged in this solution for 3 weeks. It is then tested daily for about a week against a standard buffer solution. In these tests the e. m. f. measurement is made on the cell:



Since the two calomel half-cells cancel each other, the observed e. m. f. is due to difference in pH of the solutions on either side of the glass membrane plus the "asymmetrical potential"—i. e., the potential in the glass (8, 9). An ordinary type of calomel half-cell is used in the above cell, and contact is made with the glass electrode by filling the latter completely with saturated potassium chloride solution. When the electrodes were first prepared, the asymmetric potential was found to vary, but after aging, it remained very constant in the majority of the electrodes.

If, after aging, the electrode is found to have a constant potential against a standard buffer solution (constant asymmetric potential), it is sealed to a calomel half-cell as shown in Figure 2. This half-cell is readily made by sealing a side arm of 6-mm. glass tubing into about 10 cm. of 10-mm. glass tubing, the lower end of which has had a platinum wire sealed in as shown in the figure. Near the upper end of this 10-mm. tube, a constriction is made. The glass electrode is now sealed to the side arm, after which the mercury calomel and saturated potassium chloride are added. In order to fill completely the side arm and electrode, it is necessary to apply suction occasionally to remove trapped air. After filling, the half-cell is sealed off at the constriction. Electrodes made at the same time and aged in the same way give fairly constant values with the same buffer solutions, as shown in Table I. These measurements were made on Sorensen's phosphate buffer mixtures in the range covered by this method. The results indicate that, although the apparent asymmetric potential may differ to some extent among various electrodes, the difference is independent of the pH that is measured.

TABLE I. COMPARISON OF DIFFERENT GLASS ELECTRODES FILLED WITH SATURATED POTASSIUM CHLORIDE

BUFFER pH	ELECTRODE			
	1	2	3	4
	<i>E. m. f.</i>	<i>E. m. f.</i>	<i>E. m. f.</i>	<i>E. m. f.</i>
7.78	0.022	0.022	0.030	0.026
7.53	0.033	0.034	0.044	0.039
7.38	0.043	0.044	0.053	0.049
7.18	0.053	0.054	0.063	0.059
6.87	0.072	0.073	0.082	0.078

MacInnes and associates (9, 10) have shown that from pH 1 to 9 the glass electrode described by them gives potentials which vary with the hydrogen-ion activity exactly as the hydrogen electrode. To determine if the electrode described behaved as a hydrogen electrode in the range employed in this method, potentials were taken on Sorensen's phosphate buffer solutions ranging in pH from 6.7 to 8.0. The data for two electrodes which differ in the asymmetric potential by 15 mv. are given in Figure 1. The points fall on a straight line which has the correct slope, 0.059. These data indicate that the behavior of the electrodes is quite consistent in this range of pH.

A calibration curve was prepared for the method by determining the pH of sodium bicarbonate solutions of known concentration which had been brought to equilibrium with an air mixture containing a known percentage of carbon dioxide. The air mixtures were prepared by the addition of pure carbon dioxide from a cylinder to air in a 20-liter Pyrex bottle. Acidulated water was used as a confining liquid, and each mixture was allowed to stand 2 hours with occasional shaking to allow the gas to come to equilibrium with the water. The mixture was displaced with acidulated water, passed through two Truog towers in series containing 0.1 *N* sodium hydroxide, then through a tell-tale containing bromothymol blue as an indicator, and finally measured by a gas meter. In order to reduce the error arising from the solubility of the carbon dioxide in the displacing liquid, the latter was run in quite rapidly so that the time required for a determination was about 10 minutes. The gas mixture was divided as it came from the mixing bottle and part passed through a sodium bicarbonate solution of known concentration. The sodium bicarbonate solution was prepared by diluting a standard solution of sodium hydroxide and adding carbon dioxide until a pH of about 6.0 was reached. Phenol red indicator (75 cc. of a 0.01 per cent solution per liter) was added to the sodium hydroxide solution during dilution to aid in the estimation of the end point. The apparatus used for equilibrating the bicarbonate solution is shown in Figure

2. The gas passes through the inlet *a* which is drawn to a fine point, bubbles through the sodium bicarbonate solution, and out at *b*. The presence of phenol red in the bicarbonate helps to decide when equilibrium is reached. Five minutes' bubbling at a rapid rate suffices to bring about 10 cc. of solution to equilibrium. During the aëration, the Pyrex tube containing the bicarbonate was kept in a water

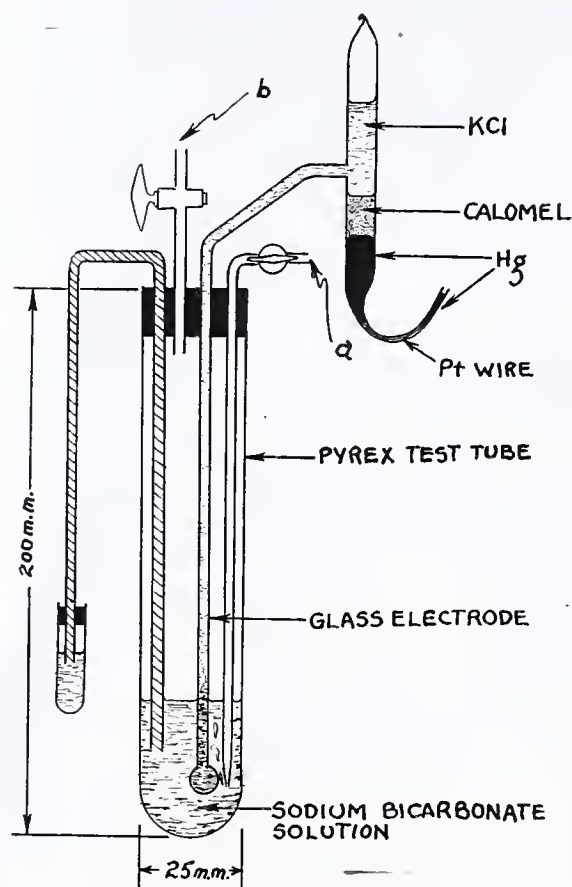


FIGURE 2. DIAGRAM OF APPARATUS

bath maintained at $26^\circ \pm 0.1^\circ \text{C.}^2$ After equilibrium was reached, the stopcocks were closed and the pH of the solution determined. It was found that the pH does not change even though the bicarbonate solution is allowed to stand 1 to 2 hours after equilibrium is reached.

After obtaining the reading on the bicarbonate solution, the electrode was checked by determining the e. m. f. of a known buffer solution. The pH of the bicarbonate solution was calculated from the formula:

$$\text{pH}_1 = \text{pH}_2 + \frac{\text{e. m. f.}_2 - \text{e. m. f.}_1}{0.0593} \text{ at } 26^\circ \text{C.} \quad (4)$$

where subscript 1 refers to the bicarbonate solution and subscript 2 to the standard buffer solution. All pH determinations were made in duplicate, and checks with 0.02 pH units were constantly obtained. The carbon dioxide in the gas was determined by a double titration modification of the official volumetric method (2). With the volume of gas passed through the towers and the temperature and pressure known, the partial pressure of carbon dioxide in the gas mixture can readily be calculated. Assuming that the concentration of the bicarbonate ion is equal to that of the sodium bicarbonate solution used and taking α_{CO_2} equal to 0.738, Equation 2 reduces to:

$$\text{pK}'_1 = \text{pH} + \log \text{pCO}_2 - 1.362$$

Fourteen determinations gave a value for pK'_1 of 6.31 ± 0.007 , indicating that the results were quite consistent.

² This temperature was used because the incubator room in which the potentiometer was set up was kept at this temperature.

From the results obtained by Hastings and Sendroy (6) at 38° C. and using $\Delta pK_1'/\Delta T = 0.005$, the value of pK_1' at 26° C. and for 0.001 *N* sodium bicarbonate concentration should be 6.375. The agreement is certainly all that could be expected in view of the differences in technic. Hastings and Sendroy determined the carbon dioxide in the gas mixtures by the Haldane apparatus, estimated the free and bound carbon dioxide in the bicarbonate solution by means of the Van Slyke apparatus, and in general made use of refinements not available to the authors. It is believed that

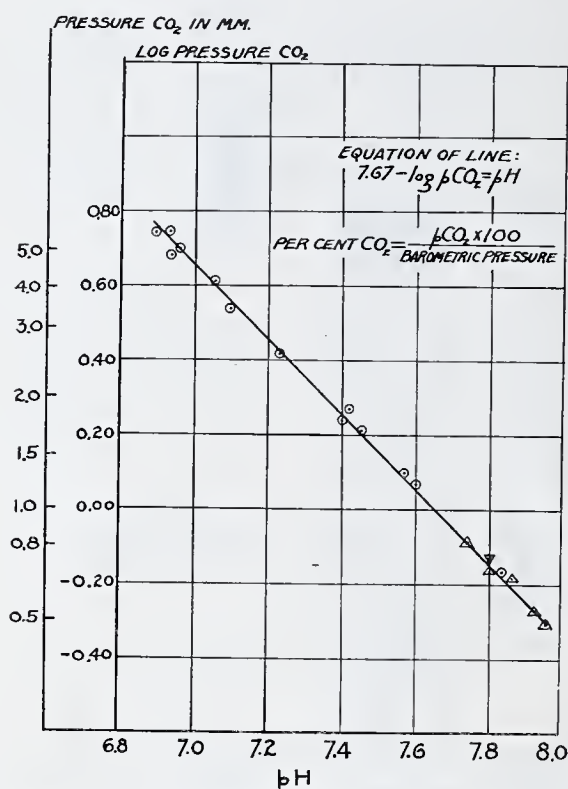


FIGURE 3. CALIBRATION CURVE FOR 0.001 *N* AND 0.0107 *N* SODIUM BICARBONATE
(For 0.0107 *N* sodium bicarbonate solution, multiply ordinate reading by 10)

use of this empirical calibration curve constructed from the results obtained under the conditions in use in the laboratory (in regard to saturation, e. m. f. measurement, etc.), is more satisfactory than would be the use of a theoretical curve based on data obtained under more ideal conditions. It is desirable that anyone adopting the method construct his own calibration curve, but if this is not possible and if the analyses are made exactly as described, the graph in Figure 3 can probably be used without introduction of appreciable error. The points located by use of the 0.001 *N* sodium bicarbonate are marked in Figure 3 by circles.

If the pCO_2 in the gas mixture is plotted against the equilibrium pH for a given concentration of sodium bicarbonate, a logarithmic curve results. For the most accurate results (speed and stability of equilibrium), it is desirable to keep the pH measurements on the part of the curve at which the curvature is greatest. This can be done by increasing the concentration of the sodium bicarbonate solution, whenever the pCO_2 is such that the pH measured lies on the flat part of the curve. Thus for mixtures containing more than 0.7 per cent carbon dioxide, it is advantageous to increase the concentration of the sodium bicarbonate solution to about 0.01 *N*. Since the theoretical pK_1' for this strength of bicarbonate is 6.34, it is necessary that a slightly stronger solution of sodium bicarbonate be used in order that the same line will represent partial pressures of carbon dioxide that are ten times as strong as those indicated by the ordinates. For example, if 0.001 *N* sodium bicarbonate is used, a pH of 7.67 represents a partial pressure of 1 mm. of carbon

dioxide. If 0.01 *N* sodium bicarbonate is used, a pH of 7.67 represents a pCO_2 of only 9.33 mm.³ Use of Equation 3 shows that if 0.0107 *N* sodium bicarbonate is used, a pH of 7.67 will represent 10.0 mm. of pCO_2 , and hence one line will serve for a ten-fold increase in concentration. The points designated by triangles were obtained by use of 0.0107 *N* sodium bicarbonate and were placed on the graph after dividing the pCO_2 by 10—i. e., subtracting 1.00 from the log pCO_2 .

METHOD

APPARATUS. The apparatus and solutions required for the determination of carbon dioxide in a gas mixture are: a glass electrode fitted in the aëration device shown in Figure 2, a potentiometer capable of measuring the pH of a solution with the glass electrode, and a standard solution of 0.001 or 0.0107 *N* sodium bicarbonate. The construction of the glass electrode has been given in detail in the text. The sodium bicarbonate solution is made by dilution of standard solution of sodium hydroxide and passing in carbon dioxide until a pH of about 6.0 is reached; phenol red indicator can be added to the solution during dilution to aid in the estimation of this end point.

PROCEDURE. For the analysis of a gas mixture containing 0.03 to 0.7 per cent carbon dioxide, about 10 cc. of 0.001 *N* sodium bicarbonate are placed in the aëration device, (Figure 2), and the mixture to be analyzed passed through at the rate of 4 to 5 bubbles per second. After approximately 5 minutes of aëration, the stopcocks are closed and the e. m. f. determined by a suitable potentiometric set-up. The pH of the bicarbonate solution is calculated from Equation 4, and the partial pressure of carbon dioxide determined from the calibration curve, Figure 3. For concentrations of carbon dioxide ranging between 0.7 and 7 per cent, 0.0107 *N* sodium bicarbonate solution is used. If the "asymmetric potential" of the glass electrode remains constant as shown by e. m. f. readings on a standard buffer solution, the calibration curve can be constructed to read pressures of carbon dioxide directly from the e. m. f. determination.

APPLICATION AND MODIFICATIONS

The method was tested by determining the carbon dioxide in gas mixtures that were used in the greenhouse; these mixtures were prepared by adding pure carbon dioxide to air, controlling the proportions of each by flowmeters. The tubes of the aëration apparatus were kept in a cheap and easily built water bath made from a large battery jar placed in a box and insulated with shavings. The temperature was maintained at 26° C. by adding cold water or by heating with a blackened 200-watt electric lamp. Temperature control of 0.1° to 0.2° C. for 10 to 15 minutes is readily obtained, and this suffices for routine analyses. At the same time that the equilibrium measurements were taken, check analyses were made by absorbing from a known volume of gas the carbon dioxide present by the method already described. The results were quite satisfactory, as the average recovery on mixtures whose carbon dioxide content ranged from 0.15 to 0.9 per cent was 103 ± 1.29 per cent. The accuracy of this method is limited by the accuracy of the pH determination, which is about 0.02 of a pH unit, corresponding to a maximum error of about 4 per cent.

Whenever a determination is made of the carbon dioxide content of an air mixture, the electrode is checked after the

³ Assuming that the pK_1' corresponding to the authors' technic would be 0.035 less than that found for 0.001 *N* sodium bicarbonate—i. e., 6.275. The mean of seven determinations of 0.0107 *N* sodium bicarbonate was 6.28 ± 0.005 , which is consistent with the values for 0.001 *N* sodium bicarbonate.

determination by means of a standard buffer solution. This added reading requires only a few minutes and serves to determine if the asymmetric potential is unchanged. Over a period of weeks, no change in two electrodes used in analysis has been observed, and hence this added determination may appear to be redundant. However, the extra labor is repaid by increased confidence in the results.

The method as described here was developed for the specific purposes of routine analyses of air samples in greenhouse work. Great accuracy was not essential for this purpose, since 5 per cent error could be tolerated. It is apparent that the method as described can be readily applied to other problems similar to this. If higher accuracy is desired, certain modifications can be made—e. g., increased accuracy of the potentiometer readings, analysis of the sodium bicarbonate solution for bound carbon dioxide content, etc. It might also be desirable to use a silver-silver chloride electrode in 0.1 *N* hydrochloric acid instead of the calomel half-cell. If the electrodes are not required to stand much shock in handling, the glass electrode described by MacInnes and Dole (9) and MacInnes and Belcher (10) might be advantageous. The calibration curve should also be determined by more refined technic, if high accuracy is desired.

Laboratories which do not have the facilities for use of the glass electrode can readily adapt the method for their needs by use of an accurate colorimetric method. With one of the newer types of pH colorimeter, an accuracy of 0.05 pH can be obtained, and this would suffice for most routine work. For example, the $p\text{CO}_2$ in an atmosphere could readily be determined by the insertion of the apparatus (Figure 2) without the glass electrode in the line supplying the gas mixture. Whenever desirable, colorimetric readings could be taken and the $p\text{CO}_2$ read from Figure 3, and in this way it would be possible to maintain a close check on the carbon dioxide content of the atmosphere. The accuracy of the results would not be as high as with the glass electrode, but a high degree of accuracy is usually achieved by the expenditure of considerable time and care. Often for routine work, ease and speed of manipulation are more desirable than the next decimal place.

DISCUSSION

It appeared to be of interest to check the results against those of other investigators who have made use of this principle for the determination of carbon dioxide. Higgins and Marriot (?), who determined the pH colorimetrically, state that they arrived at the carbon dioxide values of the pH standards used by empirical methods. An examination of the values obtained indicate that these are in great error. For example, a plot of their data (assuming a constant barometric pressure of 760 mm.) gives points that lie on a fairly straight line except at the higher concentrations of carbon dioxide. The equation of the line for 0.001 *N* sodium bicarbonate is:

$$\text{pH} = 7.42 - 0.89 \log p\text{CO}_2 \quad (5)$$

Calculations of the value of pK_1' from this line show that this "constant" varies from 5.99 to 6.12. If a barometric pressure of 740 mm. is assumed, these values are lowered slightly. The variation in the value of this constant is due to the slope of the line differing from unity. As already noted, the correct value for the constant at 26° C., according to the careful work of Hastings and Sendroy, is 6.375. Some difference would be expected if less careful technic were used, but the difference noted is larger than one might expect from mere difference in procedure and suggests that the results were subjected to a rather large systematic error. Higgins and Marriot advise use of 0.0085 *N* sodium bicarbonate for concentrations of carbon dioxide ten times as

great as those determined with the 0.001 *N* sodium bicarbonate. It has already been shown that this concentration should be 0.0107 *N*. Calculations of pK_1' for 0.0085 *N* sodium bicarbonate from Higgins and Marriot's data give values ranging from 6.05 to 6.19—i. e., values higher than with 0.001 *N* sodium bicarbonate. Reference to Equation 3 shows that this value should decrease with increasing concentration of the bicarbonate.

McClendon (11) also gives graphs showing plots of the pH of sodium bicarbonate solution of varying concentration in equilibrium with atmospheres containing carbon dioxide. He suggests a method for determining carbon dioxide in air, similar to that of Higgins and Marriot. The slopes of the lines are around 0.8, hence the values of pK_1' calculated from them vary greatly and in all cases are low. McClendon, however, states that this report is preliminary and great accuracy is not claimed for the data.

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A Composite Reagent for Calcium

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IN AN extensive study involving the determination of calcium in bone ash dissolved in dilute hydrochloric acid, a combination of some of the separate solutions used in the precipitation of calcium oxalate was found convenient.

The reagent employed is prepared by dissolving 200 grams of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) and 500 grams of ammonium chloride in 3500 cc. of water. Then 1000 cc. of glacial acetic acid and 10 cc. of 0.04 per cent methyl red are added, and if any precipitate is formed, the solution is filtered. For the amounts of calcium concerned, 50 cc. of the reagent were measured in a cylinder and added to the properly diluted calcium solution. The mixture was heated to boiling and ammonium hydroxide added to make the reaction slightly alkaline to methyl red.

This composite reagent is satisfactory for the precipitation of calcium oxalate from bone ash solutions. For use in the analysis of other materials, different proportions may be necessary. The combination of the four reagents into one solution is obviously always advantageous because of the consequent saving in time and the uniformity of procedure without loss of precision.

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Phospholipide Content of Fluid Cream

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INTEREST in the phospholipide content of various food substances has been stimulated by recent nutritional studies demonstrating the value of lecithin in the diet and by a recognition of its remarkable emulsifying powers. This has led to a desire for more exact data on the occurrence of phospholipides in fluid milk and cream. The following report covers work conducted in this laboratory on its determination in cream.

The comparatively few results reported in the literature on the phospholipide content of fluid cream show great variations. Although three phospholipides (1, 6, 7), lecithin, cephalin, and a diaminophospholipide, have been identified in cow's milk, it has been a common practice to express the total phospholipide content as distearyl lecithin. The methods used by investigators for the extraction of the phospholipide and for the subsequent determination of the phosphorus content of the extract have differed greatly. This may account in part for the lack of uniformity in results. Moreover, although the phospholipide content of cream is known to vary with the butter fat content, data reported in the literature are the results obtained with creams containing varying amounts of fat. If the reported data are calculated to milligrams of phosphorus per 100 grams of cream, assuming the lecithin when reported as such to be the distearyl type,¹ the values range from 3.62 to 13.3 mg. of phosphorus per 100 grams of cream.

A determination of the phospholipide content of fluid cream involves two major steps: (1) the quantitative removal of phospholipide from the cream, (2) the determination of the phospholipide in the extract.

The Mojonner modification of the alkaline Roese-Gottlieb procedure has been recommended for the extraction of phospholipides along with the butterfat from milk products (3, 8, 9). Whether or not all of the lecithin-like material is recovered by this procedure is still a debatable question. Petersen and Herreid (8) quantitatively recovered known amounts of lecithin which had been added to buttermilk. Chapman (3), on the other hand, was unable to recover all the added lecithin from buttermilk by this method. He does not specify the form in which the lecithin was added. In the experiment conducted by Petersen and Herreid, the lecithin was weighed into the flask containing buttermilk and was not added as an emulsion. This may account for the higher percentage recovery obtained by the latter workers. It is likely that the form in which the lecithin appears in a mixture, whether or not it is hydrated—i. e., thoroughly emulsified—plays an important part in the ease with which it is extracted.

METHOD OF EXTRACTION

Experiments conducted in this laboratory on the extraction of known quantities of lecithin from aqueous dispersion indicate that inorganic salts and possibly other materials exert definite effects on the extraction of the phospholipide. Fugii (5) found that the addition of either egg albumin or salt to an aqueous dispersion of lecithin increased the amount of lecithin extracted with ether. The combined effect of

albumin and salt, however, was not additive, owing, according to Fugii, to the formation of compounds of albumin and salt.

The source of lecithin in these experiments was a sample of commercial soy-bean lecithin (lipinol). The product contains some 30 per cent soy-bean oil, but is completely soluble in both ethyl and petroleum ether.

It is apparent from the data reported in Table I that the presence of skim milk solids² or inorganic salts increases materially the percentage recovery of lipinol from aqueous dispersion. Although small amounts of sodium and calcium chloride have been found to be carried over in the ether extracts, when these salts are added to an aqueous emulsion of lipinol, the increased recovery obtained is more than the amount of the contaminating salt. Differences of a few per cent in the latter cases, however, are not significant. Neither sodium nor potassium sulfate was found in the ether extracts. When sodium sulfate alone was added to the aqueous dispersion, the recoveries were equal to those in which both skim milk solids and sodium sulfate were added. These recoveries were 93 to 96 per cent, showing an increase of 10 per cent over the recovery without the addition of salt or skim milk solids. Since the lecithin used in these experiments was highly hydrated, the added salts together with the alcohol used in the extraction mixture probably caused a dehydration of the lecithin and thus made possible a more complete extraction with ether.

TABLE I. ROESE-GOTTLIEB EXTRACTION OF LIPINOL FROM AQUEOUS DISPERSION

SAMPLE	AMT. Gram	REACTION	SALT, 1 GRAM	RECOVERY %
Lipinol	0.1	Neutral		83.5
				83.4
				85.4
Lipinol	0.1	Neutral	NaCl	98.8
		Neutral	NaCl	101.8
		Neutral	CaCl ₂	112.9
		Neutral	CaCl ₂	98.8
		Neutral	Na ₂ SO ₄	92.6
		Neutral	Na ₂ SO ₄	92.2
		Neutral	K ₂ SO ₄	93.2
		Neutral	K ₂ SO ₄	92.3
Lipinol + skim milk solids ²	0.1 + 0.9	Neutral		89.4
		Neutral		91.6
		Neutral		89.7
		Neutral		90.8
Lipinol + skim milk solids	0.1 + 0.9	Neutral	NaCl	87.9
		Neutral	CaCl ₂	92.8
		Neutral	Na ₂ SO ₄	93.9
		Neutral	K ₂ SO ₄	89.5
Lipinol	0.1	Alkaline		83.8
		Alkaline		82.8
		Alkaline	NaCl	99.2
		Alkaline	CaCl ₂	104.6
		Alkaline	Na ₂ SO ₄	97.2
		Alkaline	K ₂ SO ₄	89.6
Lipinol + skim milk solids	0.1 + 0.9	Alkaline		90.4
		Alkaline		92.4
		Alkaline	NaCl	90.1
		Alkaline	CaCl ₂	92.0
		Alkaline	Na ₂ SO ₄	96.1
		Alkaline	K ₂ SO ₄	94.6
		Acid	NaCl	93.3
		Acid	CaCl ₂	94.6
		Acid	Na ₂ SO ₄	93.6
		Acid	K ₂ SO ₄	91.6

Other methods of extraction were attempted in an effort to find a solvent or combination of solvents which would re-

¹ The phospholipides in the extract do not consist solely of distearyl lecithin.

² Blanks on the skim milk solids were subtracted from the total extracts.

move lecithin quantitatively from an aqueous emulsion. From the data reported in Table II, it is evident that only a small amount of lecithin was extracted by petroleum ether alone or after the addition of alcohol. Extraction with alcohol and a mixture of ethyl and petroleum ether gave the best results when the concentration of alcohol was 50 per cent. Acetone was substituted for alcohol in the extraction mixture, but without a noticeable increase in the recovery of the extract. The best method of extraction, therefore, appeared to be the Mojonnier modification of the Roesse-Gottlieb procedure, after the addition of skim milk solids or inorganic salts to the dispersion.

TABLE II. EXTRACTION OF LIPINOL FROM AQUEOUS DISPERSION

ALCOHOL CONCENTRATION %	SOLVENT	RECOVERY OF LIPINOL %
20.0	Petroleum ether	2.27
33.3	Petroleum ether	2.70
42.8	Petroleum ether	2.05
50.0	Petroleum ether	23.65
20.0	Ethyl and petroleum ether	49.24
42.8	Ethyl and petroleum ether	2.52
45.0	Ethyl and petroleum ether	73.18
50.0	Ethyl and petroleum ether	71.78
55.0	Ethyl and petroleum ether	68.44
60.0	Ethyl and petroleum ether	59.37
75.0	Ethyl and petroleum ether	48.18
77.0	Ethyl and petroleum ether	51.61
80.0	Ethyl and petroleum ether	51.51
45.0	Neutral Roesse-Gottlieb	86.08
50.0	Neutral Roesse-Gottlieb	85.63
55.0	Neutral Roesse-Gottlieb	80.64
50.0	Alkaline Roesse-Gottlieb	85.03
ACETONE CONCENTRATION 50.0	Alkaline Roesse-Gottlieb	20.96

The procedure described above does not extract appreciable amounts of inorganic phosphate. Alcoholic and Roesse-Gottlieb extracts of aqueous solutions of potassium dihydrogen phosphate and calcium monophosphate were made and the phosphorus content of the extracts determined. The concentrations of inorganic phosphorus were greater than those which exist in milk or cream. It will be noted from Table III that only small amounts of phosphorus were found in the residues resulting from the alkaline Roesse-Gottlieb extractions. By use of this procedure, therefore, the amount of contaminating inorganic phosphate in an extract of cream is negligible.

TABLE III. EXTRACTION OF INORGANIC PHOSPHORUS WITH SOLVENTS

SAMPLE	AMT. Gram	METHOD OF EXTRACTION	PHOSPHORUS	
			Present Mg.	Extracted Mg.
KH ₂ PO ₄	0.05	Alkaline Roesse-Gottlieb	11.4	0.007
KH ₂ PO ₄	0.10	Alkaline Roesse-Gottlieb	22.8	0.016
CaH ₄ (PO ₄) ₂	0.05	Alkaline Roesse-Gottlieb	12.3	0.004
CaH ₄ (PO ₄) ₂	0.10	Alkaline Roesse-Gottlieb	24.6	0.016
KH ₂ PO ₄	0.05	95% alcohol	11.4	0.040
KH ₂ PO ₄	0.10	95% alcohol	22.8	0.030
CaH ₄ (PO ₄) ₂	0.05	95% alcohol	12.3	0.85
CaH ₄ (PO ₄) ₂	0.10	95% alcohol	24.6	0.90
KH ₂ PO ₄	0.05	100% alcohol	11.4	0.018
KH ₂ PO ₄	0.10	100% alcohol	22.8	0.022
CaH ₄ (PO ₄) ₂	0.05	100% alcohol	12.3	0.39
CaH ₄ (PO ₄) ₂	0.10	100% alcohol	24.6	0.81

Although the addition of sodium chloride, calcium chloride, or sodium sulfate with or without skim milk solids to an aqueous dispersion of lipinol resulted in an increase in the recovery of lipinol, the data reported in Table IV show that the addition of these salts to 40 per cent fluid cream does not alter greatly the percentage of total extract.

PHOSPHORUS DETERMINATION

After removal of the phospholipide from cream by extraction, the extract was completely oxidized and the phosphorus content of the ash determined by the method described below. Since inorganic phosphates are not extracted by the Roesse-Gottlieb procedure, at least not in sufficient quantity to affect the final result, the phosphorus content of the fatty extract is taken as a measure of the amount of lecithin or

phospholipide in the cream. The proportions of lecithin, cephalin, and sphingomyelin in the extract are not known. In fact, very little is known of the composition of milk phospholipides. The most logical expression for the phospholipide content of cream, therefore, appears to be in terms of milligrams of phosphorus per 100 grams of cream of specified fat content, or milligrams of phosphorus per 100 grams fatty extract. This avoids any assumptions for the composition of the extract or the fatty acid content of the lecithin, provided all the phospholipide is attributed to lecithin. Differences in the fat content of the cream are also eliminated when the results are reported in terms of milligrams of phosphorus per 100 grams of fatty extract.

TABLE IV. ALKALINE ROESSE-GOTTLIEB EXTRACTION OF HEAVY CREAM (6.5 TO 7.5 GRAMS)

No SALT %	NaCl, 1.0 GRAM %	CaCl ₂ , 1.0 GRAM %	Na ₂ SO ₄ , 1.0 GRAM %	Na ₂ SO ₄ , 0.7 GRAM %	Na ₂ SO ₄ , 0.5 GRAM %
38.93	38.94	38.82	39.10		
40.31		40.00	40.31		
40.33		40.16	40.21		
39.88			39.87		
39.93			39.84		
39.84			39.88		
39.79			39.84		
39.80			39.87		
40.81			40.59	40.69	40.73
40.78			40.69	40.62	40.69
40.80			40.69	40.56	40.65
40.71			40.46	40.49	40.52
40.53			40.45	40.60	40.50
40.68			40.56	40.64	40.59

A dry method of oxidation of the extract—i. e., ashing in the presence of magnesium nitrate—was adopted because of the necessity of oxidizing a comparatively large amount of fat. The addition of magnesium nitrate serves two purposes: (1) it aids the oxidation of the fat, and (2) it provides a base for binding the phosphorus. The excess magnesium nitrate is decomposed on heating, leaving magnesium oxide in the ash.

PROCEDURE

Six to seven grams of 40 per cent cream are weighed into a Mojonnier extraction flask, 1.5 cc. of concentrated ammonium hydroxide added, and the mixture extracted with alcohol, ethyl ether, and petroleum ether according to the Mojonnier modification of the Roesse-Gottlieb procedure. In the first two extractions 25 cc. of each ether are used. Three extractions are made. After evaporation of the solvents, the fatty extract is dried until constant weight is attained, and the percentage calculated. The fatty extract is then washed into a 3.5-inch (8.9-cm.) siliimanite evaporating dish (platinum dishes may be used, but siliimanite proves very satisfactory) by means of either ethyl or petroleum ether, 2 cc. of 50 per cent alcoholic magnesium nitrate added, and the mixture evaporated to dryness on an electric hot plate. The use of alcoholic magnesium nitrate and ethyl ether allows the fat and lecithin to mix uniformly with the magnesium nitrate and avoids the spattering which results with an aqueous solution of the salt. One cubic centimeter of nitric acid is then added, drop by drop, and the contents of the dish gently heated over a low flame until the mass is completely charred. It is important that the heating be done very slowly at first. The heat is gradually increased and the ashing completed in a muffle furnace. The ashing process is conducted at a sufficiently low temperature to avoid ignition. If the ash is slightly grayish or brownish in color, the addition of a few cubic centimeters of water to the cooled ash, followed by evaporation to complete dryness and a few seconds' heating, yields a white ash which is readily soluble in dilute hydrochloric acid. Just enough dilute acid is added to dissolve the ash. The solution is diluted to a volume of 20 cc. and phosphorus determined colorimetrically in 3- to 4-cc. aliquots.

Both the Briggs (2) modifications of the Bell-Doisy procedure for blood phosphorus and the Fiske-Subbarow (4) method have been used. Several determinations were carried out in which known amounts of inorganic phosphorus were added to the oxidizing agents, the samples evaporated, ashed, and phosphorus determined by both procedures. Magnesium chloride resulting from the excess magnesium nitrate did not interfere with the development of the blue color. The ash is free from other inorganic salts which cause the inaccuracies pointed out by Fiske and Subbarow. The inorganic phosphorus was recovered quantitatively. The Fiske-Subbarow reagent was freshly prepared, but the Briggs reagent was two to three weeks old at the time the first determinations were made. A week later, determinations were made on the same phosphorus solutions, using the same reagents. The following results were obtained:

PROCEDURE	P ADDED	P RECOVERED	ONE WEEK LATER
	Mg.	Mg.	Mg.
Briggs	5.0	5.00	4.98
Briggs	5.0	5.00	5.00
Briggs	5.0	4.99	4.98
Briggs	5.0	4.99	4.99
Fiske-Subbarow	5.0	5.00	4.95
Fiske-Subbarow	5.0	5.00	5.05
Fiske-Subbarow	5.0	5.00	5.00
Fiske-Subbarow	5.0	5.00	5.09

Under the described experimental conditions, neither procedure appeared to possess an advantage in so far as the accuracy of the determination is concerned. However, the Briggs procedure was adopted because it was found more convenient in running a series of determinations to make the readings 30 minutes after the reagents were added rather than after 5 minutes, as recommended in the Fiske-Subbarow method. The former reagents appear to keep better than the latter ones. This is a convenience when phosphorus determinations are made at intervals of several weeks.

In unknown samples, dilutions are such as to give readings near that of the standard. Good comparisons are made with a standard containing 0.1 mg. of phosphorus per 10 cc. If the standard is set at 25 mm., the unknowns read between 20 and 30 mm.

It is believed that the method described for the oxidation of the fatty extract does not result in the loss of phosphorus. Check determinations were made on a petroleum ether solution of soy-bean lecithin with the addition of known amounts of melted, filtered butter fat. The results are given in Table V.

TABLE V. LIPINOL OXIDIZED IN PRESENCE OF BUTTER FAT

SAMPLE	BRIGGS METHOD		FISKE-SUBBAROW METHOD	
	Butter fat	Lipinol, 0.1 gram	Butter fat	Lipinol, 0.1 gram
	Mg. P	Mg. P	Mg. P	Mg. P
Butter fat + 0.1 gram of lipinol	0.08	2.31	0	2.36
	0.08	2.31	0	2.34
	0.09	2.37	0	2.44
	0.08	2.36	0	2.40
	Av. 2.34 \pm 0.03			
0.1 gram lipinol (aqueous)		2.30		
		2.35		
		2.45		
		2.37		
	Av. 2.37 \pm 0.04			

From aqueous solution, the average value is 2.37 mg. of phosphorus per 0.1 gram of lipinol, or 2.37 per cent as compared with 2.34 mg. of phosphorus per 0.1 gram of lipinol (2.34 per cent) in the presence of 3 grams of butter fat. This difference is within the experimental error.

PHOSPHOLIPIDE CONTENT OF FLUID CREAM

The phospholipide content of a number of samples of heavy cream is given in summary in Table VI. The uni-

form values obtained indicate that approximately the same percentage of phospholipide is extracted from all samples having approximately the same butter fat content. Inasmuch as the addition of sodium sulfate to the samples of cream reported in Table IV did not result in an increase in the per cent of extract from the cream, sodium sulfate was not added to the samples reported in Table VI. Actually, the addition of sodium sulfate to cream increases the phosphorus content of the extract slightly, as shown by the following data from two experiments:

CREAM SAMPLE	FATTY EXTRACT %	PHOSPHORUS	
		Extract, 100 grams Mg.	Cream, 100 grams Mg.
1	39.14	18.3	7.2
1 + Na ₂ SO ₄	39.18	18.9	7.4
2	39.01	17.9	7.0
2 + Na ₂ SO ₄	39.02	18.6	7.2
		Av. 18.2 \pm 0.38	Av. 7.2 \pm 0.10

The average value for the samples of cream reported in Table VI is slightly higher than the average value for the above samples. The latter experiments were conducted on a winter cream, as contrasted with the cream reported in Table VI which was produced in the late summer and early fall. Although the difference may be indicative of a seasonal variation, the data are too meager to consider the difference significant. In all cases, however, the wide variations reported in the literature have not been observed.

TABLE VI. PHOSPHOLIPIDE CONTENT OF FLUID CREAMS

FATTY EXTRACT %	PHOSPHORUS	
	Extract, 100 grams Mg.	Cream, 100 grams Mg.
40.35	21.2	8.5
40.06	19.4	7.7
39.87	20.5	8.0
39.67	18.8	7.4
40.70	19.7	8.0
41.94	20.5	8.5
40.27	19.2	7.6
40.53	20.4	8.2
40.57	19.7	7.9
40.79	19.7	8.0
40.11	20.0	8.0

Av. 19.9 \pm 0.55 Av. 8.0 \pm 0.24

Each figure represents the average of two to four determinations on the same sample of cream. If the ashing is carefully carried out at a slow rate, duplicate determinations check within 0.1 to 0.5 mg. of phosphorus per 100 grams of cream.

EXTRACTION OF LIPINOL FROM CREAM

In an attempt to determine the percentage recovery of phospholipide from cream, 0.2 and 0.4 per cent of soy-bean lecithin were added to heavy cream, the modified alkaline Roese-Gottlieb extraction made with and without the addition of sodium sulfate, the fatty extracts ashed, and the phosphorus content of the ash determined. The results are given in Table VII.

The results in Table VII show that at least the major part of the phospholipide occurring normally in cream is recovered by the described procedure. The addition of sodium sulfate to the cream before extraction increases the recovery only slightly. The addition of the salt becomes more important, however, as the phospholipide content of the cream is increased. The per cent of fatty extract may not be materially affected, but the amount of lecithin-like materials in the extract is greater in every case. Therefore, to insure the maximum recovery of phospholipide from cream, sodium sulfate should be added before the extractions are made.

Forty per cent cream was dried at 70° C. under reduced pressure, and a Soxhlet extraction with absolute alcohol

made. Since inorganic phosphates are appreciably soluble in alcohol, the alcoholic extracts were concentrated under reduced pressure, the residues taken up with petroleum ether and filtered before the extracts were ashed. The following values compared with the Roesse-Gottlieb extraction of the fluid cream resulted:

SAMPLE	PHOSPHORUS/100 GRAMS OF CREAM	
	Roesse-Gottlieb extraction	Alcohol extraction
	Mg.	Mg.
Control cream	7.9	6.8
Cream + 0.2% lipinol	11.6	10.1
Cream + 0.4% lipinol	15.2	16.1

The phospholipide content of the control sample of cream which was extracted with alcohol is lower than any value obtained heretofore. The values for the samples containing 0.2 and 0.4 per cent lipinol are scarcely better than those obtained by direct extraction of the fluid cream and require a much longer time for completion.

The Mojonner modification of the Roesse-Gottlieb procedure for the extraction of fat has been found the most feasible and effective method for the removal of phospholipide from fluid cream. This procedure extracts the major part of the lecithin-like materials and is far more practical than an alcoholic extraction of the dried cream. It does not extract measurable amounts of inorganic phosphorus.

Phospholipides may be completely oxidized in the presence of comparatively large amounts of fat by direct ashing, if an excess of base is present and the ashing is done at a very low temperature at the beginning.

The phospholipide content has been found to be very uniform and lies between 18 and 20 mg. of phosphorus per 100 grams of fatty extract for cream produced in New York State during the late summer and early fall. There is a slight indication of a small seasonal variation. It is recom-

mended that phospholipide content be expressed in terms of milligrams of phosphorus per 100 grams of extract.

TABLE VII. RECOVERY OF LIPINOL FROM FLUID CREAM

	FATTY EXTRACT %	PHOSPHORUS/100 GRAMS OF CREAM		RECOVERY %
		Found	Calcd. ^a	
		Mg.	Mg.	
Control cream	40.17	7.9		
Cream + 0.2% lipinol	40.07	11.6	12.5	92.8
Cream + 0.4% lipinol	40.08	15.2	17.1	88.8
Control cream	39.14	7.2		
Control cream + 0.7 grams Na ₂ SO ₄	39.18	7.4		
Cream + 0.2% lipinol	39.14	10.7	11.8	90.6
Cream + 0.2% lipinol + 0.7 gram of Na ₂ SO ₄	39.16	11.4	12.0	95.0
Cream + 0.4% lipinol	39.10	14.7	16.4	89.9
Cream + 0.4% lipinol + 0.7 gram of Na ₂ SO ₄	39.00	15.7	16.6	94.6
Control cream	39.10	7.0		
Control cream + 0.7 gram of Na ₂ SO ₄	39.02	7.3		
Cream + 0.2% lipinol	38.89	10.6	11.6	91.3
Cream + 0.2% lipinol + 0.7 gram of Na ₂ SO ₄	39.00	11.4	11.9	95.8
Cream + 0.4% lipinol	38.95	15.1	16.2	93.2
Cream + 0.4% lipinol + 0.7 gram of Na ₂ SO ₄	38.98	15.5	16.5	93.9

^a 0.1 gram of lipinol \approx 2.3 mg. of phosphorus.

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New Molecular Weight Micromethod

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IN VIEW of the simplicity and ease of operation of the Victor Meyer method of determining molecular weights, it was considered desirable to adapt the apparatus to the use of micro samples, and to simplify somewhat its construction. Since the accurate measurement of the volume of a micro sample in the vapor state would present some difficulty, it was decided to employ the change in pressure of an isothermal system before and after vaporization of the substance as an index of the molecular weight, the volume of the system being known. Several pieces of apparatus for molecular weight determination have been described (1, 2, 3) which operate on a similar principle, but all of them are inefficient or complicated, and none employs truly micro samples.

CONSTRUCTION OF APPARATUS

The final form of the apparatus is as shown in Figure 1, which is self-explanatory. It is essentially an inner jacket, *A*, fitted with a mercury manometer; the inner jacket is surrounded by an outer jacket, *B*, to maintain constant temperature during a determination. The outer jacket is constructed from a 25 by 200 mm. Pyrex test tube, a 200-mm. side arm, *J*, of 5-mm. tubing being fused on as shown to serve as a condenser for the vapors of the heating medium. The inner jacket is made from a 15 by 150 mm. test tube. A 40-mm. length of 4-mm. tubing is fused to the bottom of the test tube, and three short lengths of thin rod, *C*, are sealed equi-

distant around the circumference of the tube about 10 mm. from the sealed end. These rods should be of such length that the inner jacket will be centered in the outer jacket when the apparatus is assembled. A 50-mm. length of the 4-mm. tubing is fused to the upper end of the test tube.

A Pyrex stopcock, *D*, which has a bore of 1.5 to 2 mm., is sealed to the upper end of the inner jacket. The plug of the cock should be well ground, and the channel of the plug should coincide with the channel of the barrel of the cock, in order that an unobstructed passage of at least 1.5 mm. be made through the stopcock. A short distance below the seal, an 80-mm. length of capillary tubing, *E*, of 0.5-mm. bore is sealed to the inner jacket, and the end bent downward as shown. A 100-mm. length of 5-mm. tubing is fused to the end of the capillary with a neat joint at *F*. A short length of 5-mm. tubing, *G*, is fused to the manometer arm as shown, and sealed off to a 15-mm. length. This trap serves to retain any air bubbles that may rise up the manometer tube. A reference mark for the mercury in the manometer is etched around the side arm about 4 mm. below seal *F*, as shown in Figure 1. Before use, the inner jacket is filled with water to the reference mark to ascertain the volume of the inner jacket.

The apparatus is now assembled as shown in Figure 1. An asbestos board, *N*, with a hole of just the right size to admit outer jacket *B*, is used to prevent superheating of vapor

in *B*. The inner jacket is supported in the outer jacket by means of a split cork stopper. A 300-mm. reference scale, *H*, completes the apparatus. A stopcock, *L*, fitted with a short length of pressure tubing, *K*, and a length of thick-walled tubing, *M*, is also provided. Its use will be described later.

DETERMINATION OF MOLECULAR WEIGHTS

In case the substance whose molecular weight is to be determined does not decompose at temperatures 20° to 30° C. above its boiling point under atmospheric pressure, the procedure is relatively simple. Melting point tubes 50 mm. in

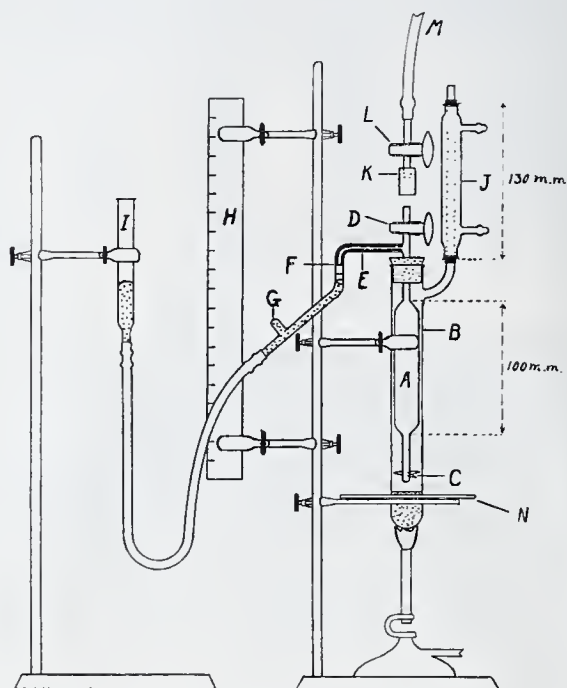


FIGURE 1. ASSEMBLED APPARATUS

length and of such diameter to slip rather easily through the bore of stopcock *D*, are used to contain the samples. A tube of the correct dimensions is dried carefully and weighed on the microbalance. A sample of 2 to 10 mg. is pipetted into the tube with a micropipet, large sample weights being used when the molecular weight anticipated is large. The tube is then heated gently at a point about 10 mm. from the open end over a microflame to distil back into the tube that part of the liquid adhering to the central portion. That part of the liquid from the heated portion of the tube to the open end is distilled out, of course. Now the tube is heated more strongly and is drawn out into a capillary about one-third the original diameter of the tube, as shown in *a*, Figure 2. The upper end of the constriction is heated with the pointed flame of a blast lamp until the tube closes and a bead of glass is formed which will not pass through the plug of *D*. When completed, the sealed tube resembles *b*, Figure 2. The open end of the sample tube is now passed through the flame to make certain that all liquid has been removed from that portion of the tube. The sample tube is cooled and weighed on the balance. It has been found that no error due to vaporization of glass occurs in this method of sealing the sample tubes.

A liquid with boiling point 15° to 20° C. above that of the sample is chosen as the heating medium. It is poured into *B* to such depth that the liquid level will be at least 10 mm. below the end of the inner jacket. The manometer is filled with mercury, and the inner jacket is tilted to fill trap *G*. The inner jacket is placed in position inside *B*, stopcock *D* is closed, and the burner under *B* is lighted. The liquid in

B is boiled just vigorously enough to insure *B*'s being filled at all times with vapor. It has been found convenient to wrap *B* with asbestos paper to minimize condensation. The level of the mercury in the right hand manometer arm is brought to the reference mark, and *D* is closed. If the level drops, *D* should be opened until *A* will come to the temperature of *B*. When no change in mercury level is noted when *D* is closed, the determination may be begun. Equilibrium is usually established within two minutes after the heating liquid begins to boil.

D is now opened and the sample tube inserted, the tube projecting downward into *A* with the bead resting on the upper end of the plug channel, thus preventing the tube from dropping into *A*. The mercury level is brought to the reference mark and the level of the mercury in bulb *I* is read off on scale *H*, estimating to 0.2 mm. *D* is closed, thus breaking the capillary of the sample tube and allowing the tube to drop to the bottom of *A*. As the sample vaporizes, the leveling bulb is raised to keep the mercury in the side arm approximately at the reference mark. When there is no further increase of pressure in *A*, the mercury level in the side arm is adjusted to the reference mark and the level of the mercury in the leveling bulb is read off. The difference in the initial reading and final reading of mercury levels gives the change of pressure within *A*. *I* is lowered, the plug of *D* is removed, a long capillary tube is inserted into *A*, and the vapor of the sample is removed by suction. *A* is now removed, and the temperature of the vapor bath determined. The treatment of results will be described below.

In case the compound tends to decompose at its atmospheric boiling point, the initial pressure within *A* may be lowered sufficiently to allow vaporization of the sample at a temperature below the decomposition point. In such a case, the final pressure within *A* will still be below atmospheric. In fact, it is often desirable to start below atmospheric pressure, even in the case of compounds that do not decompose at their boiling points, allowing the use of a heating vapor not over 10° C. above the boiling point of the substance. In addition, the inner jacket may be filled with an inert gas to hinder decomposition. To start below atmospheric pressure requires the use of the auxiliary stopcock, *L*.

When the sample tube has been inserted in *D*, the top of *D* is lightly greased with vaseline and *L* is connected by means of the pressure tubing, *K*. *L* is closed and *M* is connected with the vacuum line. *I* should be lowered sufficiently to place the mercury level in the side arm of *A* to some point just above trap *G*. *L* is opened slowly, and as the mercury level rises in the side arm, *I* is lowered until the mercury level is from 100 to 200 mm. below *F*. *L* is then closed, and the mercury level in the side arm brought to the reference mark. If the mercury level remains constant, the level of the mercury in *I* is recorded on *H*, the sample tube broken by turning *D*, and the determination completed as previously described. Calculations in this case will be identical in procedure with the first case.

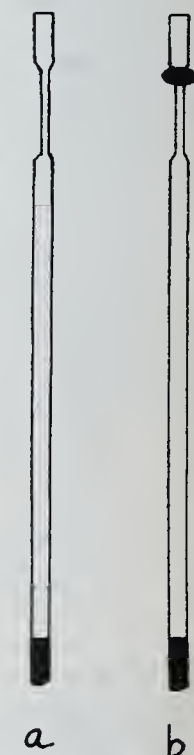


FIGURE 2. METHOD OF SEALING SAMPLE TUBES

CALCULATION OF CONSTANT FOR APPARATUS

The molecular weight of a substance may be calculated from the following equation, adapted from that of Lumsden (3):

$$\text{M. W.} = \frac{22410 \times 760 \times T \times W}{1000 \times 273 \times V \times \Delta p}$$

where T = absolute temperature of vapor bath
 W = weight of sample taken, mg.
 V = volume of inner jacket, ml.
 Δp = change of pressure within A , mm.

Collecting constants, the above equation becomes:

$$\text{M. W.} = K \times \frac{T \times W}{\Delta p}$$

It is apparent that the constant, K , of any apparatus may be calculated, once the volume of the inner jacket is known.

DISCUSSION

The average accuracy of the method is within 2.5 per cent; with accurate estimation of pressure change, the error is usually lower. Table I illustrates some typical results obtained with the apparatus; some of the data were first trials of students in a class of advanced organic chemistry. As the sample can be weighed out in less than 15 minutes, and the vaporization requires less than 5 minutes, the entire deter-

mination can be made in 20 minutes with accuracy comparable with the large Victory Meyer apparatus.

TABLE I. TYPICAL MOLECULAR WEIGHT DETERMINATIONS

COMPOUND	B. P. ° C.	(Constant for apparatus, 3.059)		ΔP mm.	M. W. FOUND	M. W. CALCD.	ERROR %
		TEMP. OF BATH ° C.	WT. OF SAMPLE Mg.				
$\text{C}_4\text{H}_{10}\text{O}_2$	134.7	140.0	6.605	95.0	87.8	90.1	-2.5
		140.0	6.624	94.0	89.0	90.1	-1.2
C_6H_6	80.4	99.6	3.704	53.5	78.9	78.1	+1.0
		99.6	5.977	88.0	77.4	78.1	-0.9
CCl_4	76.0	100.5	5.540	41.0	154.4	153.8	+0.4
		100.5	4.591	33.5	156.6	153.8	+1.8
CHCl_3	61.2	100.5	6.074	57.3	121.1	119.4	+1.4
		100.5	6.087	57.5	121.0	119.4	+1.3
CH_3COCH_3	56.5	100.5	1.754	34.0	58.9	58.1	+1.4
		100.5	8.087	160.8	57.4	58.1	-1.2

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Note on Measurement of Activity of Commercial Invertase

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THE enzyme invertase is now on the market in extremely active form in aqueous solution preserved in glycerol. It is used in the food industries for the inversion of cane sugar, especially to prevent crystallization. Its action in cream centers and fondant coatings, in which the slow inversion caused by the invertase offsets the tendency of the sucrose to crystallize, has recently been described by Paine (5).

Our knowledge of the laws of its action is due to O'Sullivan and Tompson, Hudson, Nelson, Willstätter, and to many others; information on the solubility relations of sucrose, invert sugar, and water at equilibrium has been published by Jackson (3). We still lack, however, a rapid, convenient, and exact method for measuring the activity of commercial invertase. The unimolecular reaction constant has been used extensively as a means of measuring invertase activity. Nelson (4) showed conclusively, however, that the reaction does not follow the unimolecular law, except under unusual conditions, but that the unimolecular constant values steadily increase during the course of the inversion.

The method described below is offered as a contribution to the problem. It is based on the method used by Hudson and Paine (2), and the activity is expressed in a similar manner. It differs from it essentially in that an arbitrary reaction time has been selected. Ammonia is used in terminating the inversion, as suggested by Bayliss (1), avoiding on the one hand the uncertainty incident to the use of dry sodium carbonate, and on the other the possibility of destruction of the sugar by use of excessive amounts of strong alkali.

The sample of invertase is diluted fifty-fold with water—e. g., 2 grams are diluted to 100 cc. Of the diluted sample, 5 cc. are placed in a flask and 50 cc. of sucrose solution added at 20° C., with the time noted using a fast-running 50-cc. pipet. (The sucrose solution contains per liter 100 grams of cane sugar and 40 cc. of Walpole acetate buffer of 4.6 pH; 10.2 cc. of 1 *N* acetic acid and 9.8 cc. of 1 *N* sodium acetate diluted to 100 cc.) The solution is then incubated at 20° C. for a 50-minute interval, when 0.5 cc. of strong

ammonia is added. The solution, after standing for a few minutes, is polarized at 20° C. in a 2-decimeter tube.

The initial polarization is determined by polarizing at 20° C. a mixture of 5 cc. of the diluted sample, 0.5 cc. of strong ammonia, and 50 cc. of the sugar solution, mixed in the order named.

The activity K_{50} is evaluated by the formula

$$K_{50} = \log \frac{a}{a-x}$$

where a is the calculated range through which the polarization changes upon complete inversion by invertase, and x is the fall in polarization observed. The value a is calculated from the formula

$$a = \frac{P'}{100} \times \left(141.7 - \frac{t}{2}\right)$$

where P' is the original polarization, P , corrected for the zero reading of the polariscope, and t is the temperature. Example: The initial reading was 34.8° V. The zero reading of the polariscope was 0.5° V. The reading after the 50-minute digestion period was 18.0° V.

$$\text{Then } a = \frac{34.8 - 0.5}{100} \times 131.7 = 45.17^\circ \text{ V.}$$

$$x = 34.8 - 18 = 16.8^\circ \text{ V. and } K_{50} = 0.20$$

Thus, the activity is simply the unimolecular reaction constant calculated at the 50-minute interval and multiplied by the dilution.

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Determination of Reducing Sugars

Application of Shaffer and Hartmann Iodometric Cuprous Titration

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SHAFER and Hartmann (6) have reported that the iodometric cuprous titration could be adapted to the determination of reducing sugars by the use of Fehling-Soxhlet solution and the amounts and conditions of heating prescribed by Munson and Walker (3). Using the Munson and Walker tables for the conversion of copper into terms of sugar, they have obtained substantially correct values for the sugar present when the equivalence factor of 6.36 mg. of copper per cc. of 0.1 *N* sodium thiosulfate was used. However, from previous investigations conducted in this laboratory, by others as well as the writers, this theoretical factor seemed too low to give complete recovery of sugar. Therefore we have undertaken to determine if such is the case, and, if possible, to determine the cause.

Munson and Walker have demonstrated the accuracy of the direct weighing of cuprous oxide so that the chief source of difference between the results obtained by the procedure as carried out by Shaffer and Hartmann and that prescribed by Munson and Walker apparently is due to the difference in conditions of reduction used. Shaffer and Hartmann did not strictly adhere to the conditions of heating prescribed by Munson and Walker. The solutions were heated in a 300- or 400-cc. Erlenmeyer flask covered with a small beaker instead of in a 400-cc. beaker covered with a watch glass. Quisumbing (5) and others (1, 2, 7) have shown that the type of container used for reduction affects the results obtained.

TABLE I. COMPARISON OF LATERAL AREA AND TOTAL AREA OF CONTAINERS OF VARIOUS TYPES

CONTAINER	DIAM. Cm.	LATERAL AREA TO LIQUID IN CON- TAINER		SURFACE OF LIQUID TO AIR		TOTAL AREA OF LIQUID TO GLASS
		HT. OF LIQUID EXPOSED TO GLASS	AREA OF BOTTOM SURFACE	HT. OF LIQUID EXPOSED TO AIR	AREA	
400-cc. beaker	7.5	2.4	56.6	44.2	44.2	100.8
300-cc. Erlenmeyer	8.7	2.1	50.5	35.3	59.5	85.8
400-cc. Erlenmeyer	9.2	1.9	55.6	39.6	66.5	95.2
500-cc. Erlenmeyer	9.7	1.7	55.2	41.9	73.9	97.1

Quisumbing shows "that when the action of air is excluded, reduction is proportional not to *total* but to *lateral* area of liquid exposed to the glass." He believes that this relationship is due to the fact that as the reduction proceeds the cuprous oxide formed drops from the sides of the container to the bottom, thereby decreasing the accelerating action of the glass along the bottom, leaving the free surface along the sides for catalytic action. A comparison between total area and lateral area of a number of containers is shown in Table I. It is seen there that the lateral area of the liquid exposed to glass is approximately the same in the 400-cc. beaker and the 500-cc. Erlenmeyer flask, so that if this is the controlling factor the substitution of the flask for the beaker should not markedly affect the results. However, owing to the increased surface area exposed to air in the flask, there is more danger from loss of cuprous oxide by oxidation.

ANALYTICAL PROCEDURE

The dextrose used in these determinations was obtained from the Bureau of Standards. It was weighed against brass weights in air, and transferred to calibrated volumetric flasks.

The solutions were made to volume at room temperature (22.5° C. average), and a record was kept of the temperature. The chemicals used were the purest that could be obtained on the open market. Stock solutions were made up in only 4-liter lots according to the procedure recommended by Munson and Walker, and Shaffer and Hartmann. The thiosulfate solution was adjusted to exactly 0.1 *N* at 22.5° C. against recrystallized potassium dichromate. It was stored in a 10-liter Pyrex stock solution bottle and was preserved with a few cubic centimeters of carbon disulfide. Blank determinations on the stock solutions were frequently run and showed only slight variations. The 500-cc. Pyrex Erlenmeyer flasks and 400-cc. Pyrex beakers used in these tests were carefully selected to have the same distribution of glass by choosing flasks or beakers of the same weight.

It was found that, as reported by Shaffer and Hartmann, it was necessary to dissolve the cuprous oxide precipitate completely in the presence of the iodate-iodide solution after acidification, and subsequently to dissolve the cuprous iodide formed in order to obtain close agreement between duplicate or triplicate determinations. It was found that the cuprous

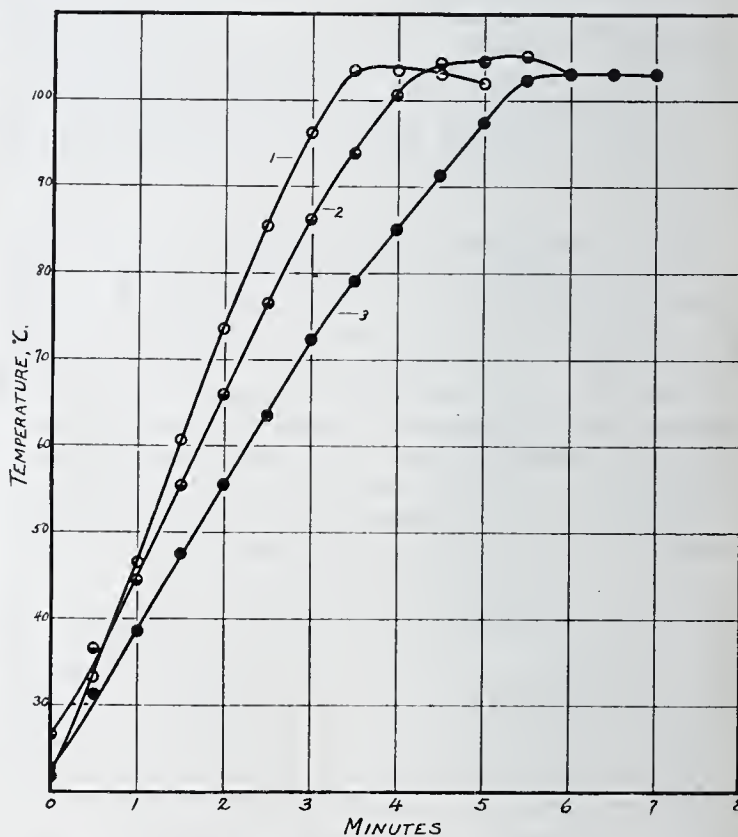


FIGURE 1. RATE OF TEMPERATURE CHANGE OF 100 CC. OF SOLUTION IN ERLERMAYER FLASK

Flame adjusted to bring solution to boil in (1) 3 min., (2) 4 min., (3) 5 min.

iodide precipitate dissolved more readily in the presence of a large excess of iodine than when but a slight excess was present. When the solutions were cooled to from 35° to 40° C., the solution of both precipitates was rapid, but at about 20° C. the precipitates dissolved with difficulty. The end point in the titration of solutions cooled to temperatures below 35° C. were somewhat obscured by a precipitation which occurs, apparently composed of tartrates.

DISCUSSION

EFFECT OF BOILING CONDITIONS. Quisumbing (4) has shown that changes in barometric pressure affect the amount of copper reduced by reducing sugars when the Munson and Walker technic is used. He has also shown that the temperature of boiling under their conditions is not constant, ranging from 101° to 105° C. depending on conditions of heating.

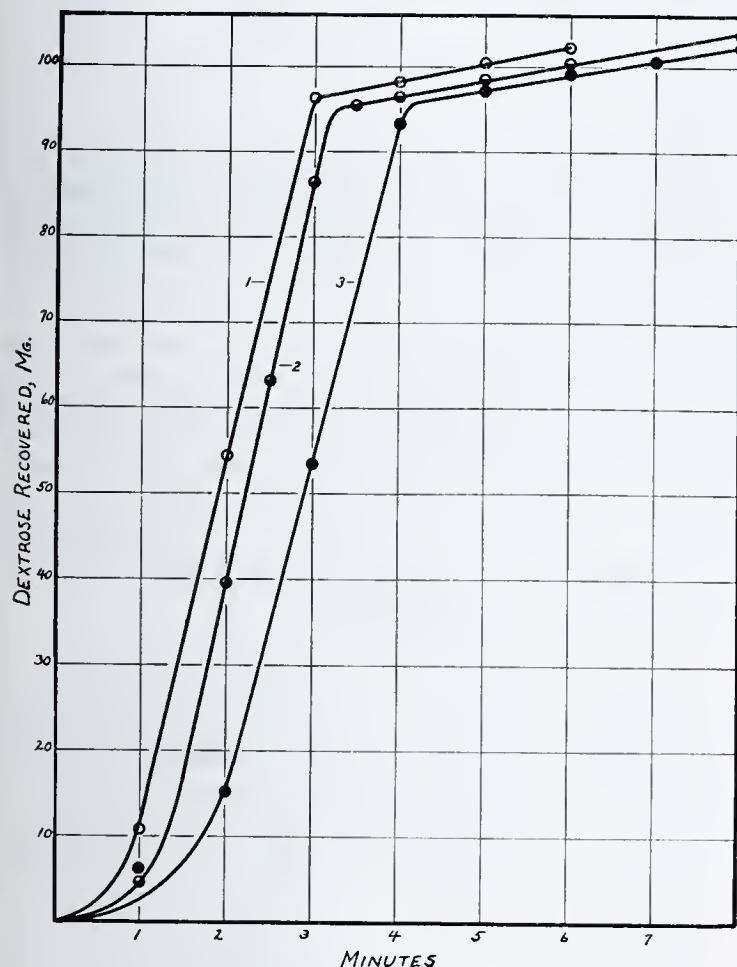


FIGURE 2. EFFECT OF HEATING CONDITIONS ON RECOVERY OF DEXTROSE

Flame adjusted to bring solution to boil in (1) 3 min., (2) 4 min., (3) 5 min.

In carrying out the reduction both in Erlenmeyer flasks and in beakers superheating was found to occur with such regularity that it is almost impossible to decide when to begin to reckon the time of boiling. It was impossible to obtain triplicate determinations agreeing within 0.6 mg. of copper on samples when some had superheated to varying degree and extent during boiling, and when some had not superheated. It was thought that glass beads (4 mm. in diameter) placed in the flask would reduce the danger of superheating. In addition to covering the flask with a 50-cc. inverted beaker, it was thought that covering with a small funnel might allow the release of steam pressure more freely than the heavier water-sealed beaker. Slight improvement resulted from the use of the funnel alone, but superheating still persisted, making it very difficult to obtain checks with triplicate determinations. Leaving the flask uncovered, however, almost completely stopped the superheating. The glass beads prevented superheating when used in either an uncovered or covered flask.

The results shown in Table II indicate that superheating is of considerable importance in the determination. The determinations in which superheating occurred gave values which exceeded the actual amount of dextrose present. The covered flask containing 20 glass beads was very close to the actual, whereas the uncovered flask containing glass beads was below the actual, probably owing to surface oxidation

caused by increase in the surface of the liquid exposed by the more vigorous boiling. Where the glass beads are used, there is a vigorous agitation of the cuprous oxide precipitate causing it to rise and drop back to the bottom of the flask. In the uncovered flask without beads in which the liquid boils without superheating, such agitation does not occur. The boiling is less vigorous, the cuprous oxide precipitate does not rise to the surface of the liquid, and surface oxidation is reduced.

TABLE II. EFFECT OF BOILING CONDITIONS ON OXIDATION OF DEXTROSE BY FEHLING'S SOLUTION

(100 mg. of dextrose per determination)

TREATMENT	THIO-SULFATE TITRATION ^a Cc.	Cu REDUCED Mg.	DEXTROSE RECOVERED Mg.
Uncovered 500-cc. Erlenmeyer containing 20 glass beads	6.07	197.86	99.76
500-cc. Erlenmeyer covered with 50-mm. funnel with 20 glass beads	5.92	198.81	100.21
Uncovered 500-cc. Erlenmeyer	5.84	199.32	100.47
500-cc. Erlenmeyer covered with 50-mm. diameter funnel	5.81	199.51	100.58
500-cc. Erlenmeyer covered with 50-cc. beaker	5.67	200.40	101.08

^a Figures represent average of at least three determinations which varied by not more than 0.1 cc.

Glass beads, although alleviating superheating, are objectionable for other reasons. During the titration they tend to increase the crystallization of tartrates. Although this does not interfere with the reaction, it does interfere slightly in securing a sharp end point. For reasons given, the remaining tests reported for Erlenmeyer flasks were carried out in uncovered containers.

COMPARISON OF BEAKER AND FLASK. A comparison of the relative extent of recovery of dextrose when reduction was carried out in Erlenmeyer flasks and in covered beakers is shown in Table III. The Shaffer and Hartmann procedure was followed, using both the flask and beaker with the same dextrose solution. The determinations were carried out at the same time so that the conditions of heating would be identical for the two. Quadruplicate determinations were run in the tests, while "blanks" were run in duplicate at the conclusion of each test.

The analyses show that consistently higher results were obtained with the beaker, also in all instances except the 50-mg. sample, the milligrams of dextrose found are higher than the actual amount contained in the sample. The lower amount of dextrose recovered in the flasks was probably due either to increased surface oxidation of the cuprous oxide precipitate, since they were uncovered, or to the superheated condition prevailing in the covered beakers, causing an increased yield of reduced copper. It can safely be concluded from the results that the uncovered Erlenmeyer flask can be used in the method to give yields which are very close to the actual amount of dextrose present.

TABLE III. COMPARISON OF BEAKER AND FLASK AS RECEPTACLES

DEX-TROSE PER 25-CC. ALI-QUOT Mg.	BEAKERS ^a			ERLENMEYER FLASKS ^b		
	Thio-sulfate titration Cc.	Cu reduced Mg.	Dextrose recovered Mg.	Thio-sulfate titration Cc.	Cu reduced Mg.	Dextrose recovered Mg.
50.0	20.87	101.83	49.87	21.13	101.63	49.75
100.08	5.40	199.77	100.73	5.81	199.07	100.34
150.12	28.92	291.35	151.17	29.17	290.08	150.47
200.16	15.47	376.89	201.29	15.82	374.99	200.20

^a 400 cc. capacity, 7.5 cm. in diameter.

^b 500 cc. capacity.

RATE OF REDUCTION OF FEHLING'S SOLUTION BY DEXTROSE. It was observed that during the heating process there was a definite time at which the reduction of Fehling's solution by dextrose became visible, as noted by a change from the clear dark blue of the unheated liquid to a cloudy bluish red liquid. The time at which this change occurred

TABLE IV. RATE OF REDUCTION OF FEHLING'S SOLUTION BY DEXTROSE OVER FREE FLAME ADJUSTED TO BOIL IN TIME INDICATED
(100 mg. of dextrose per determination)

TIME Min.	BOILING IN 3 MIN.			BOILING IN 4 MIN.			BOILING IN 5 MIN.		
	Thiosulfate titration ^a	Cu reduced	Dextrose recovered	Thiosulfate titration ^a	Cu reduced	Dextrose recovered	Thiosulfate titration ^a	Cu reduced	Dextrose recovered
	Cc.	Mg.	Mg.	Cc.	Mg.	Mg.	Cc.	Mg.	Mg.
1	33.57	23.02	10.93	35.56	10.30	4.72	35.16	13.03	6.05
2	19.69	111.30	54.66	24.30	81.92	39.90	32.23	31.67	15.05
3	7.09	191.44	96.30	10.01	172.80	86.48	20.04	109.20	53.55
4	6.35	196.14	98.81	7.09	191.37	96.26	8.00	185.78	93.30
5	5.81	199.58	100.50	6.37	195.95	98.70	6.87	193.27	97.25
6	5.34	202.57	102.24	5.84	199.32	100.47	6.30	196.59	99.06
7							5.80	199.77	100.72
8				4.93	205.11	103.85	5.38	202.44	102.17
2.5				17.07	127.90	63.10			
3.5				7.34	189.78	95.42			

^a Figures represent averages of triplicate determinations.

varied slightly with the amount of dextrose in the sample; the temperature was about 70° C.

The rate of reduction of Fehling's solution by dextrose was determined at minute intervals on 100-mg. samples with the flame of the gas burner adjusted to cause boiling in 3, 4, and 5 minutes. The rate of heating of the dextrose-Fehling's solution mixture was determined by the use of a mercury-in-glass chemical thermometer with a range of 10° to 110° C., graduated at 2° C. intervals. In most cases ten runs were made at each flame adjustment using the different flasks employed in the determinations.

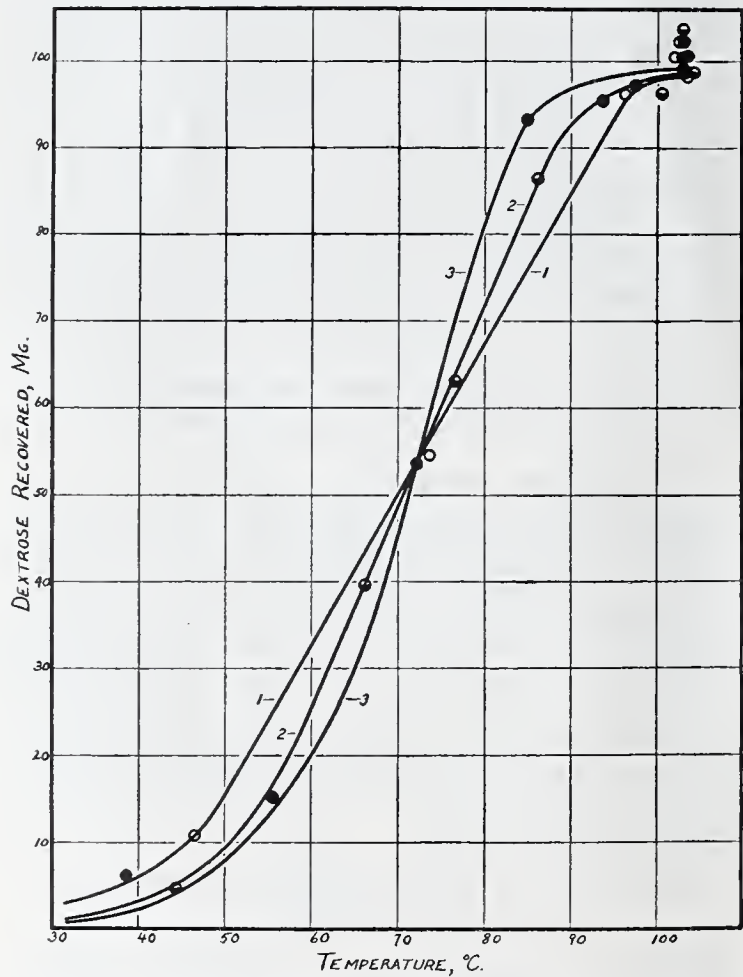


FIGURE 3. EFFECT OF TEMPERATURE ON AMOUNT OF DEXTROSE RECOVERED DURING HEATING
Flame adjusted to bring solution to boil in (1) 3 min., (2) 4 min., (3) 5 min.

The method used in determining the rate of reduction of the Fehling's solution consisted of adjusting the flame so that boiling began at the times indicated. The dextrose solution containing 100 mg. per 25 cc. of aliquot was pipetted, over as short a time interval as possible, into enough Erlenmeyer flasks so that triplicate determinations could be made at minute intervals from the start of heating up to and including 3 minutes of boiling. After adding 25 cc. of distilled water and 25 cc. of Fehling's A and B, the samples were placed on

the flame, allowed to remain there for a given time interval, removed, and plunged into a cooling bath of running water at a temperature of 15.6° C. The flasks were rotated in the cooling bath for 30 seconds and then allowed to stand in water for 2 minutes. It was found that the temperature of the boiling solution could be reduced to 45° C. at the end of the 30-second interval. Each member of a complete series was heated and cooled before the samples were subjected to the regular iodometric titration procedure of Shaffer and Hartmann.

The results of these determinations are tabulated in Tables IV and V and are shown graphically in Figures 1, 2, and 3.

TABLE V. RATE OF HEATING OF DEXTROSE-FEHLING'S SOLUTION MIXTURE OVER FREE FLAME ADJUSTED TO BOIL IN TIMES INDICATED

TIME Min.	(100 cc. of solution per 500-cc. Erlenmeyer flask)		
	BOILING IN 3 MIN. ° C.	BOILING IN 4 MIN. ° C.	BOILING IN 5 MIN. ° C.
0:00	22.0	26.7	22.8
30	33.2	26.7	31.2
1:00	46.7	44.4	38.7
30	60.7	55.6	47.5
2:00	73.7	66.1	55.5
30	85.5	76.7	63.5
3:00	96.2	86.1	72.2
30	103.5	93.9	79.0
4:00	103.5	100.6	85.0
30	103.0	104.2	91.2
5:00	102.0	104.4	97.5
30		105.6	102.2
6:00		103.0	103.0
30		103.0	103.0
7:00		103.0	103.0
30		103.0	
8:00		103.0	

Figure 1 shows the rate of heating of the solutions under the conditions specified. The curves follow the averages of the points obtained. It will be seen that there is a change in slope in each of the curves at approximately 70° C., corresponding to the time at which the reduced cuprous oxide first becomes visible. This is probably owing to a change in the rate of heat transfer caused by the cuprous oxide formed.

Figure 2 shows the milligrams of cuprous oxide formed with the flame adjusted to cause boiling at 3, 4, and 5 minutes, respectively. It is seen that enough cuprous oxide is formed in the preliminary heating to boiling to give 96 to 99 per cent recovery of dextrose regardless of the time of the heating period. At the end of 2 minutes of boiling, complete recovery is obtained regardless of the time required to heat the solution to boiling. The curves also show a steady increase in the amount of copper reduced to cuprous oxide by dextrose with increase in the time of boiling. Apparently the essential factor in the procedure of heating used by Munson and Walker is not the time necessary to bring the solution to boiling, but the time elapsed from the start of boiling until the flask is removed and cooled by immersion in a cold water bath. Munson (2) and Walker evidently realized this to be the case, but did not give data to support the selection of their particular procedure. In his preliminary work, Munson showed that the reduction was from 99 to 99.5 per cent complete at the time boiling starts, using the amounts of copper recovered after 2 minutes of boiling as 100 per cent. His

data also show that reduction proceeds at a steady rate for at least 4 minutes after boiling starts.

From our data it is safe to conclude that the preliminary heating period is of minor importance and that the time should be reckoned from the start of boiling and continued for exactly 2 minutes in order to secure accurate results by the use of Munson and Walker tables. At sea level the time of boiling should be reckoned from the time the solution first reaches 102.5° C.

Figure 3 shows the relation of milligrams of dextrose recovered to the temperature. It will be seen that the reduction of Fehling's solution by dextrose is a function of both the time and temperature with the flames adjusted to cause boiling in the times indicated. Two interesting points are shown by the graph. All three curves intersect at a common point, showing approximately 50 per cent reduction at a temperature of 70° C. This is the point in the preliminary

heating period where the reduction first becomes visible. The curves again come together at a temperature between 102° and 103° C., corresponding to the boiling point of the solution at which the reduction is from 96 to 99 per cent complete.

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Use of Metallic Lithium in Analysis of Gases

Determination of Nitrogen in Inert Gases

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HELIUM of approximately 97 per cent purity is produced in this country by the liquefaction of natural gas, the remaining impurities being mainly nitrogen, with small percentages of argon and oxygen, together possibly with some water vapor from the storage cylinder. Determination of the purity of the helium offers difficulties when a rapid and accurate one with more than one gaseous impurity present, is desired. If we assume a mixture of two gases only, a number of more or less satisfactory methods for determining the purity may be employed. Thus, the Edwards balance (1) measures the density of the gas mixture, but requires a trained operator and the use of an expensive precision instrument. The use of the viscometer (2) requires a thorough knowledge of the properties of the gases involved, and also an appreciation of the limitations of the apparatus; the device, furthermore, is not very sensitive. The katharometer (3) is excellent as a recording purity meter, but in practice it has been found that it cannot be completely trusted without periodical calibration. The charcoal adsorption apparatus as arranged by H. P. Cady is probably the most accurate and sensitive instrument in use. However, considerable time is required for each determination, and the apparatus is elaborate. Furthermore, a supply of liquid air, which may not always be available, is necessary.

If the impure helium under test is known to contain oxygen as well as nitrogen, and the air-nitrogen ratio is not in a definite and known proportion, the problem becomes more difficult. Of the devices mentioned, only the Cady instrument does not require that the composition of the impurities be known. The others measure some property of the helium as modified by the presence of a known impurity, and the purity of the helium is derived thereby.

APPARATUS

A device has been constructed which uses metallic lithium to form nonvolatile compounds with nitrogen, oxygen, and water vapor contained in a given volume of impure helium, and from the change in pressure produced by the removal of

these gases the purity is calculated. The device does not distinguish helium from the other rare gases, but if the contamination of the helium has been due to admixed air (resulting from its use in balloons) the determination of the nitrogen content becomes a matter of first importance rather than the detection of very small quantities of argon or neon which may be present.

The apparatus, which has been quite satisfactory in analyzing samples, is shown in Figure 1. A 400-cc. round-bottomed Pyrex flask is supplied with three capillary stopcocks sealed to the bottom; one leads to a capillary manometer, another to a high-vacuum pump, and the third to the source of gas sample. Since lithium must be heated to the melting point before rapidly combining with the nitrogen—owing to protective action at room temperature of the surface film—a heating element is introduced. This consists of a small resistance coil similar to that in an ordinary automobile cigar lighter. The current is conducted through heavy wires supported by a Pyrex tube held firmly in a rubber stopper. The outer end of the tube is sealed gas-tight with de Khotinsky cement. The heating element serves the dual purpose of supplying heat and supporting a small shallow boat of sheet iron containing the lithium.

PROCEDURE

A small piece of lithium is introduced into the boat and the stopper is tightly inserted. The flask is thoroughly evacuated and the tightness of the apparatus is confirmed by comparing the manometer reading with the barometric height. The sample of gas to be analyzed is next admitted slowly into the bulb. When the sample to be taken is part of a stream flowing constantly through a train of apparatus, it is convenient to allow the analyzer to fill slowly so that but a small fraction of the gas current is withdrawn for analysis, the rest being vented through a trap or bubble tube. When the flask has filled to the desired pressure, say 550 mm., the stopcock admitting the gas is closed and the manometer reading again taken. Current is then applied, conveniently derived from a small transformer. As the

lithium melts it rapidly absorbs oxygen and nitrogen. Although the removal of the water vapor by molten lithium with the production of relatively nonvolatile products is complete after sufficient time, it will usually be preferable to remove water vapor by passage of the gas through suitable absorbents and to carry out the analysis of the dry gas in the analyzer. The time required in heating usually is not over 2 minutes, but depends on the amount and character of the impurities present. In any case, until experience is gained, it is well to reheat the lithium until it is known that absorption is complete.

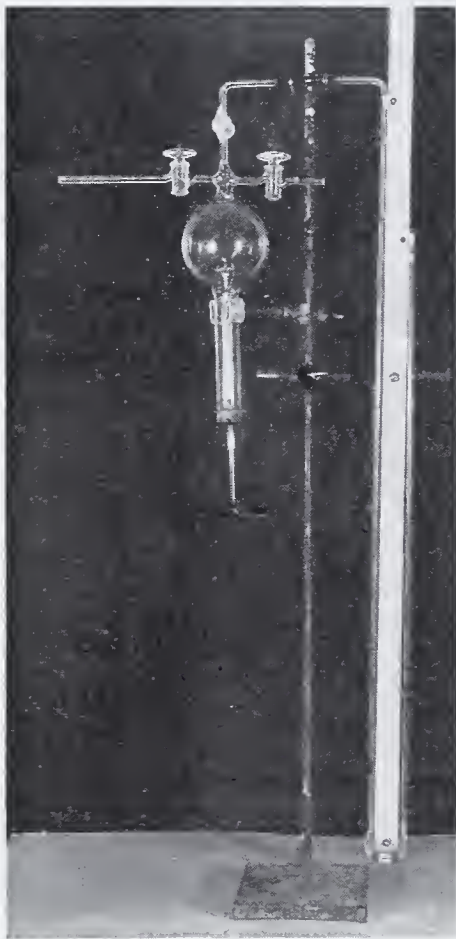


FIGURE 1. APPARATUS FOR DETERMINING PURITY OF HELIUM

When the current is cut off, the gas cools completely in about 10 minutes owing to the high thermal conductivity of helium. When equilibrium is reached, as shown by constancy of the manometer readings, the pressure, now being due to helium only (together with argon, if present), is again recorded. The second pressure divided by the first is the fractional purity of the sample. The room temperature during the period of a single determination in general will not vary by a significant amount, so that thermostating of the analyzer is quite unnecessary in order to attain reasonable accuracy.

Tests show that impurities are quantitatively removed, and that sensitivity and accuracy are limited chiefly by the reading of the manometer. Measured volumes of dry air, dry nitrogen, and water vapor were introduced separately into measured volumes of fairly pure helium, giving a known percentage purity of the mixture. The purity of the helium employed was qualitatively determined by the examination of the spectrum. The presence of argon, nitrogen, oxygen, and water vapor was reported, as well as the absence of hydrogen. The absence of carbon dioxide was determined by independent tests.

A quantitative analysis gave the following results:

	%
Water vapor (absorption by P ₂ O ₅)	0.17
Oxygen (absorption by hot Cu)	0.41
Nitrogen (absorption by hot Li)	3.03
Total impurities	3.61

Argon was present as a trace only and so neglected. The analysis, therefore, shows the helium used to be 96.39 per cent pure. To check this, a density determination was made, the average molecular weight of the impurities being taken as 28.0. By this method the helium was determined 96.42 per cent pure.

Known mixtures were tested in the lithium analyzer; series of representative results are given in Tables I to IV.

TABLE I. TEST OF KNOWN MIXTURES

				%	
			Helium	96.39	
			Impurities:		
			Nitrogen	3.03	
			Oxygen	0.41	
			Water vapor	0.17	

TABLE II. TEST OF HELIUM-NITROGEN MIXTURES

NITROGEN PRESENT %	PRESSURE BEFORE REACTION Mm.	PRESSURE AFTER REACTION Mm.	PRESSURE DUE TO IMPURITIES Mm.	NITROGEN FOUND %
0.98	510	505	5	0.9 ₁
2.35	510	498	12	2.3 ₆
3.40	530	512	18	3.4 ₀
5.22	536	508	28	5.2 ₀
10.21	539	484	55	10.2 ₀

TABLE III. TEST OF HELIUM-DRY AIR MIXTURES

DRY AIR PRESENT %	PRESSURE BEFORE REACTION Mm.	PRESSURE AFTER REACTION Mm.	PRESSURE DUE TO IMPURITIES Mm.	DRY AIR FOUND %
1.17	513	507	6	1.1 ₇
2.54	531.5	518	13.5	2.5 ₁
3.15	508	492	16	3.1 ₅
10.27	526	472	54	10.2 ₃

TABLE IV. TEST OF HELIUM, NITROGEN, OXYGEN, AND WATER VAPOR MIXTURES

—IMPURITIES PRESENT—				PRESSURE BEFORE REACTION Mm.	PRESSURE AFTER REACTION Mm.	IMPURITIES FOUND %
Nitro- gen %	Oxy- gen %	Water %	Total %			
3.01	0.39	1.81	5.21	585	554.5	5.2 ₁
2.92	0.38	3.76	7.06	556	517	7.0 ₁
0.00	0.00	100.00	100.00	17.5	0.0	100.0 ₀

The reactions of lithium with nitrogen, oxygen, and water vapor are complete for all practical purposes at temperatures attained in the apparatus, and the compounds formed are nonvolatile at ordinary temperatures. Carbon dioxide, which is in part reduced by lithium to carbon and in part to carbon monoxide, must be removed by appropriate absorbents before the gas is admitted to the analyzer.

The possibility of reactions taking place in the cold, especially in the case of water vapor, was considered, as this would affect the result, possibly materially. In no case, even with water vapor alone, was any reaction detected over a period of 5 minutes in the analyzer. Apparently the surface film which covers lithium in the air even after being freshly cut is sufficient to retard any reaction in the cold. In one case the analyzer was evacuated completely, and then water vapor to a pressure of 17.5 mm. was admitted. This was allowed to stand at room temperature to determine whether the vapor reacted with lithium to form hydroxide and liberate hydrogen with a consequent change in volume, and therefore a change of pressure: $2\text{Li} + 2\text{H}_2\text{O} \longrightarrow 2\text{LiOH} + \text{H}_2$. After standing 5 minutes without heat, no change of pressure was noticeable. When the lithium was heated to melting, the reaction proceeded rapidly, and within one minute the pressure within the flask had fallen to zero. It is evident that molten lithium removes water vapor completely, with formation of hydride and hydroxide.

With the manometer used for the above tests, it was considered that each leg could be read to within 0.25 mm., making a maximum error on each recording of 0.5 mm. Using an initial mixture pressure of above 500 mm., the maximum error of each determination was considered not more than 0.1 per cent.

ACKNOWLEDGMENT

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Determination of Hydrophyllic Colloid Content of Cane Juice

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THE ability of certain plants to resist droughts and others to resist low or freezing temperatures has long interested scientific observers. Gortner (1) and Newton (4) and later Newton and his co-workers (5) explain the resistance of plants to the desiccating effect of drought or low temperatures as due to their ability to hold water in a "bound" condition by means of hydrophyllic colloids which the resistant plants or varieties have elaborated. They believe the hydrophyllic colloids in Xerophytic plants prevent excessive moisture losses during severe desiccation such as is induced by periods of drought. Likewise, in the case of winter hardy plants, which are not killed by temperatures considerably below 0° C., these colloids prevent streaming of water from the interior of the cells to the intercellular spaces where it may form ice crystals and injure the plant. It has been previously shown that the type of material of which these colloids are composed is probably polysaccharides, such as pentosans in the case of drought-resistant plants, and protoplasmic proteins in the case of frost-resistant plants. However, since both of these classes of substance may act as hydrophyllic colloids, we may use the same mechanism for measuring both these phenomena.

Any method, then, which will measure either the amount of hydrophyllic colloids in the plant or the amount of water bound by these colloids will be of value in increasing our knowledge of the physical conditions of the constituents of the plant sap. This knowledge may be of value also as a means of distinguishing those varieties of canes which are the most resistant to low temperature. Also, any increase in our knowledge of the conditions of the colloids in cane juice may be of value in sugarhouse practice. With these objectives in view, investigations were undertaken in the fall of 1930 in an attempt to determine the cold resistance of the various new varieties of sugar canes which have been introduced into Louisiana within the past few years.

In 1922 Newton and Gortner (4) proposed a method for determining the per cent of bound water in plant juice, which is based upon the observation that the depression of the freezing point of a plant juice, upon the addition of sufficient sucrose to make a molal solution of it in the total water present in the juice, is greater than the theoretical amount which should be obtained. This excess depression they explain on the assumption that all the water in the juice is not free to dissolve the sucrose, and therefore the actual concentration is somewhat greater than the apparent molal concentration. The assumption is also made, based upon Scatchard's (6) work, that sucrose in molal concentration forms the hexahydrate. If sucrose hexahydrate is formed in solution, then we will have one mole of sucrose hexahydrate dissolved in 1000 - (18 × 6) or 892 grams of water, which gives a depression of 2.085° C. instead of the value 1.86° C. In their original paper, Newton and Gortner use

the following formula for calculating the grams of bound water:

$$\text{Bound water} = \frac{dT_0 - (dT_1 + Km)}{dT_0 - dT_1} \times 892 \quad (1)$$

where dT_1 = freezing point depression of freshly expressed juice
 dT_0 = freezing point depression of juice after addition of sucrose

Km = 2.085° C. on basis that sucrose forms hexahydrate

In a later publication Newton and co-workers (5) have modified this formula by changing the value of Km from 2.085° C. to the value experimentally obtained by determining the freezing point of a molal solution of the sucrose in distilled water. This change was found necessary because the various lots of sucrose used gave values for molal solutions somewhat higher than this theoretical value of 2.085° C.

In applying the method of Newton and Gortner to cane juices, several correction factors must be introduced. By determining the freezing points of sucrose solutions of varying concentrations, the increments of increase of the freezing point with increasing amounts of sucrose in solution are not constant. This is brought out in Table I.

TABLE I. FREEZING POINTS OF SUCROSE SOLUTIONS

SUCCESSIVE ADDITIONS OF SUCROSE	SUCROSE ADDED Mole	AV. INCREASE IN FREEZING POINT DEPRESSION DUE TO 0.25-MOLE SUCROSE ° C.
1st	0.25	0.546
2nd	0.25	0.533
3rd	0.25	0.533
4th	0.25	0.543
5th	0.25	0.555
6th	0.25	0.562
7th	0.25	0.572
8th	0.25	0.583

Accordingly the depression of the freezing point of sucrose solutions has been plotted against concentration, as shown in Figure 1. Then by knowing the sucrose content of the cane juice, by use of the graph, the depression of the freezing point due to the sucrose present in the juice can be obtained. Likewise the depression of the freezing point can be determined for the total amount of sucrose after the addition of a mole of sucrose. By this means then, errors due to the fact that the freezing point depressions of sucrose solutions are not directly proportional to concentration can be eliminated. By the use of this method it will be noted that the freezing point of the original juice has been divided into two factors: that due to the sucrose present, and that due to the nonsucrose solutes.

A second correction must be introduced as pointed out by Moran and Smith (3) and applied by Grollman (2), and one which Newton and Gortner failed to take into consideration. However, the correction of Grollman—i. e., multiplying dT_1 by 1000/892—cannot be applied successfully to juices

which are high in sucrose, such as cane juice, or even some samples of winter wheats which may contain as high as 6 per cent sucrose.

As mentioned previously, the abnormally high depressions of the freezing points of sucrose solutions are explained on the basis that the sucrose is hydrated. This means, then, that sucrose is removing water from solution. In a cane juice, which contains solutes other than sucrose, the addition of sucrose to the juice will cause the nonsucrose solutes to be dissolved in an amount of water different from that in which they were dissolved in the original juice. Since the

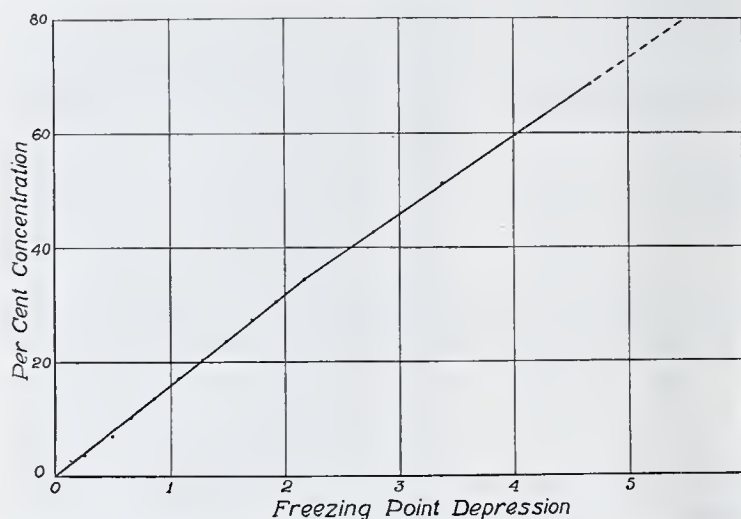


FIGURE 1. DEPRESSION OF FREEZING POINT OF SUCROSE SOLUTIONS vs. CONCENTRATION

degree of hydration of sucrose varies with the concentration, a graphical method was also used in making this correction for changes in the amount of solvent water. Figure 2 was obtained by plotting depressions of the freezing point of sucrose solution against amount of solvent water, which can be readily calculated by using the formula:

$$\text{Solvent water} = \frac{1.86 \times 1000 \times M}{dT_M}$$

where M = molal concentration of sucrose
 dT_M = depression of freezing point of sucrose solution of M concentration

The depression of the freezing point due to the nonsucrose solutes can now be corrected for changes in the amount of solvent water caused by the addition of sucrose to the cane juice. This can be calculated as follows:

$$dT_2 = (dT_1 - dT_4) \times W_1/W_2$$

where dT_2 = depression of freezing point of non-sucrose solutes corrected for sucrose change in solvent water

dT_1 = depression of freezing point of original juice

dT_4 = depression of freezing point due to sucrose in original juice

W_1 = amount of solvent water in original juice

W_2 = amount of solvent water after addition of one mole of sucrose to juice

The formula for calculating bound water then becomes:

$$\text{Grams bound water} = \frac{dT_0 - (dT_2 + dT_3)}{dT_0 - dT_1} \times W_2 \quad (2)$$

where dT_0 = freezing point depression after addition of sucrose

dT_1 = freezing point depression of juice

dT_2 = freezing point depression of nonsucrose solutes corrected for change in solvent water

dT_3 = freezing point depression due to total sucrose present after addition of one mole of sucrose

W_2 = grams free water in juice after addition of sucrose

The experimental determinations were carried out on samples of juice obtained from the various new varieties of canes which have been introduced into Louisiana. The juice was expressed from representative samples by means of an

experimental mill. The brix, sucrose content, freezing point depression of the original juice and the juice plus a definite amount of sucrose were determined on each sample. The freezing point determinations were made using the Beckman set-up, the usual precautions being observed. The samples were collected beginning October 27 to December 12.

TABLE II. AVERAGE VALUES OF BOUND WATER

CANE	Av. SUCROSE %	BOUND WATER			Total
		Formula 1	Formula 2	Sucrose	
P. O. J. 36	8.79	38.3	12.7	143	155.7
P. O. J. 36M	10.20	48.8	14.0	125	139.0
P. O. J. 213	10.10	42.0	10.0	133	143.0
C. O. 281	17.00	50.2	15.4	121	136.4
P. O. J. 234	11.60	45.5	11.6	125	136.6
C. P. 807	12.00	45.3	12.0	127	139.0

Since the values of bound water for a given variety of cane varied rather widely for samples collected during the season, the average values have been tabulated and are shown in Table II. There is no apparent correlation between bound water content and the ability of the various varieties to withstand frosts or freezing temperature as calculated by this method (Formula 2). Since Newton and Gortner have shown a correlation between winter hardiness and bound water for wheat plants, their formula (Formula 1) was applied to the data without again showing any correlation.

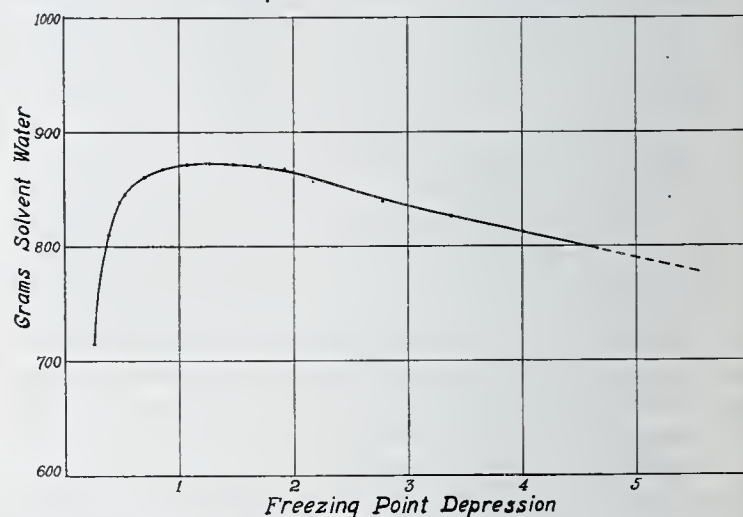


FIGURE 2. DEPRESSION OF FREEZING POINT OF SUCROSE SOLUTIONS vs. AMOUNT OF SOLVENT WATER

The amount of water of hydration of the sucrose in the original juice is also included in the table. The amount of water held by the sucrose is tremendously greater than that held by the colloids. In the last column is tabulated the total bound water content. Although these values are in the approximate order of hardiness of the cane varieties toward frost, there is not sufficient difference between them to be significant. It appears as a logical explanation, then, that the production of sucrose by plants as cold weather approaches is an extremely effective means of protection. For the cane plant, at least, we need not postulate the production of colloids, since the production of sucrose is equally as effective if not more so. This is borne out by the rapid increase in sucrose content and purity with the advent of low temperatures in the fall.

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Collecting Train for Recovering Traces of Iodine from Ashed Samples

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IN CARRYING out determinations of iodine in minute amounts in large samples of organic material, in ashing apparatus of the McClendon or Pfeiffer type (7,9-13), it is necessary that the iodine in the gaseous combustion products be collected in some kind of train. The type of train usually used has contributed to the difficulty of the analysis in a number of ways. Its interference with the egress of combustion products from the apparatus complicates the burning process. The elimination of the liquid and solid reagents contained in the train, as must be done before the final determination is made, adds to an already cumbersome procedure. The use of large amounts of reagent in a few recommended types of train, some of which is difficult to render iodine-free, offers the possibility of introducing a considerable correction for the blank determination.

The collecting train described herein was devised to collect iodine with a minimal interference with the gas stream and without the use of large amounts of liquid or solid reagent. It may be employed with any type of ashing device in which the stream of evolved gas is sufficiently slow, such as the wet ashing method of Pfeiffer or the ashing bulb previously described by the writer (3). Figure 1, showing the assembled apparatus with such a bulb, and Figure 2, illustrating individual parts of the apparatus, make a detailed description unnecessary. The function of each part, however, will be discussed briefly.

OPERATION OF APPARATUS

A normal operation of the apparatus is without the development of any back pressure. The manometer, therefore, is inserted into the system to serve as a warning device only. The activating mechanism for the Cottrell precipitators is similar to that described by other authors on iodine analysis (8). The coils in the last three collecting tubes are made from No. 20 nichrome wire by wrapping it about a rod of such size that the finished coil will fit tightly between the input tube and the wall of the collecting tube. They are stretched till there are about ten turns to the inch before being wrapped about the inner tube and inserted in their proper place. These coils undergo very little corrosion except when nitrogenous materials are burned. The salts resulting from this corrosion cause no difficulty in the final determination when the alcohol-potassium carbonate extraction method is used in concentrating

the sample. The coils are present to facilitate heat exchange between the tube and the gas. For this purpose, other materials than nichrome would undoubtedly serve better, but the particular coils described are satisfactory for reasons herein-after indicated, and at the same time are low in cost. Rubber connections and rubber stoppers are used throughout the entire train, with the usual precautions to expose as little rubber as possible to the gas stream.

The first tube serves to condense most of the moisture of combustion. With it is caught considerable solid smoke. The packing of glass wool assists in bringing smoke and moisture into contact. In this first tube from 32 to 37 per cent of the iodine is collected from representative samples.

The second freezing tube removes most of the remainder of the moisture. This step is necessary in order that the gas stream will not be saturated with water when it reaches the first Cottrell precipitator. It is also essential to avoid the freezing-shut of the third collecting tube.

The precipitator as illustrated, under the conditions herein described, is adequate for collecting the solid material which has passed through the glass wool in the first condensing tube from most types of sample. In some samples, however, in which the mineral content is quite high, this precipitator is rendered ineffective by the deposited material in the latter part of runs on 60-gram samples. In such cases it is well to have available a second precipitator connected into the system in parallel, by means of a three-way stop-cock and T-tube. The amount of iodine caught in the precipitator is governed largely by the form in which it occurs and by the mineral constituents present with it. The amount usually runs from 3 to 8 per cent of the total. Whether or not the precipitators may be eliminated from the system, as has been done by some investigators, depends on the nature of the samples and the familiarity of the operator with them. It is the author's experience that the precipitator illustrated is more easily cleaned than a tower containing beads or glass wool that may be substituted for it.

The third collecting tube immersed in acetone and solid carbon dioxide collects 38 to 50 per cent of the total iodine, and the second similar tube 3 to 8 per cent. When samples containing considerable nitrogen are burned, nitrogen dioxide is frozen out in these last two collecting tubes. Care must be taken to neutralize this condensed material before the tube has warmed completely, lest elemental iodine be swept out with the expanding vapors.

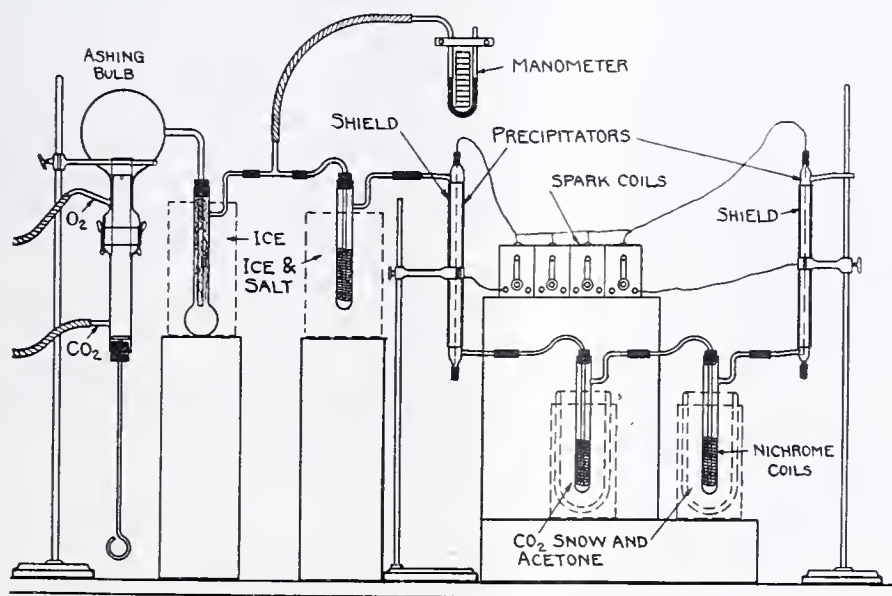


FIGURE 1. ASHING APPARATUS AND COLLECTING TRAIN

The final precipitator is appended as a precautionary measure and in a normal run collects very little material.

The train at the end of the run contains nothing but precipitated solid ash and the condensable products of the combustion. These combustion products are washed from the train with water containing sufficient potassium carbonate to assure distinct alkalinity in order that the iodine will be retained during concentration and subsequent treat-

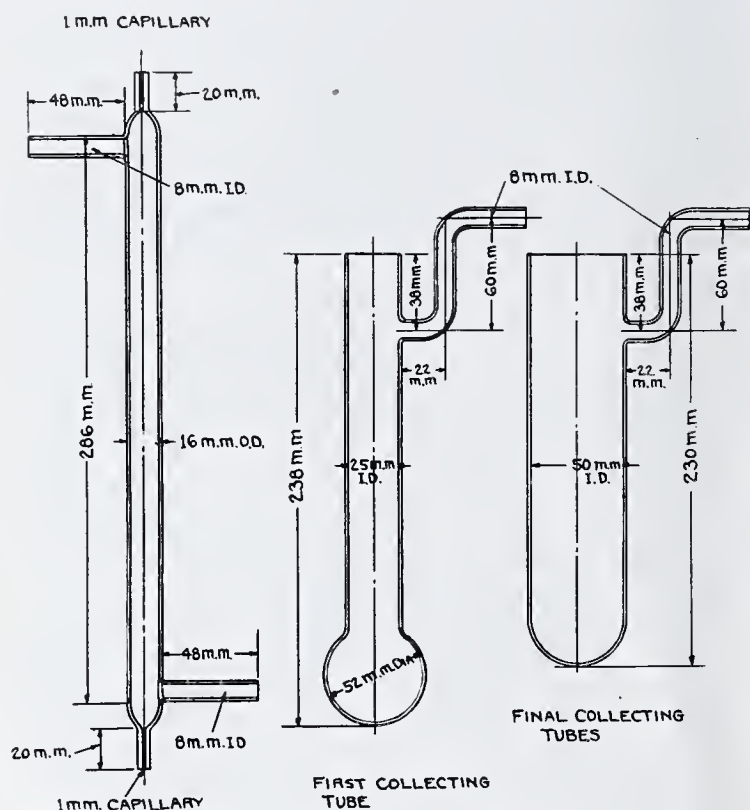


FIGURE 2. PRECIPITATOR

ment. The entire washings from the train and from the bulb type of ashing apparatus previously described usually amount to about 300 cc.

The efficiency of collection in this type of train is dependent to a considerable extent on the speed of the gas stream. The latter, in turn, is dependent on the initial oxygen-input rate, the completeness of oxygen utilization, the amount of condensable combustion products, and the cross section of the gas stream in the selective portions of the apparatus. The recovery of approximately 90 per cent, using an oxygen input of 1.4 liters per minute, although no higher than that reported using other types of train, is considerably more consistent than that obtained with other types in the author's experience. The recoveries made with the train are consistently higher on samples of food materials and animal tissues than determinations made by the open-dish ashing method using controlled temperatures. This observation is interesting in view of the fact that the open-dish ashing technic used gave good recoveries of potassium iodide.

TABLE I. RECOVERY DETERMINATIONS OF IODINE

ACCOMPANYING MATERIAL	IODINE CONTAINED IN PULP		IODINE ADDED	IODINE FOUND	IODINE RECOVERED	
Grams	γ/kg.	γ	γ	γ	γ	%
6.5	280	1.8	106	98.2	96.4	90.9
6.2	280	1.7	106	97.2	95.5	90.0
18.0	750	13.5	20	31.8	18.3	91.5

NOTE. Determinations were made by the titrimetric method after oxidation with iodine-free (4) bromine.
The Greek letter γ is used for 1 microgram (= 0.001 mg.).

Examples of recovery determinations of iodine added as potassium iodide to samples of paper pulp made with the collecting train described are shown in Table I.

LIMITATIONS OF APPARATUS

A collecting train of this type has certain inherent limitations which it is well to point out. Under ideal operating conditions, the limit of recovery in any train is set by the vapor pressure of the pure products in the train, the partial pressure of the products in solution, and the volume and approach to saturation of the emerging gas. In those types of train using reagents, the desired products are converted to compounds which have negligible vapor pressure at room temperature. In the train described, the collected materials are modified only as the products of combustion act as reagents, the effectiveness of collection depending on the fact that the vapor pressure of the products is negligible at the temperatures attained in the collecting tubes. We are dealing with a number of possible iodine compounds as products, whose actual nature is dependent largely on the original state of combination and the nature of the other material in the sample. At the temperature of combustion we would expect that, in the absence of basic metals, most of the iodine would be released as the free element, both hydrogen iodide and oxides of iodine being unstable at elevated temperatures. Most of the metallic iodide salts would probably be decomposed as well. The basic products capable of being volatilized on assuming the form of dust beyond the elevated temperature zone might recombine with iodine to give iodides and oxy-salts of iodine. These products would condense and settle in the system, dissolve in the water of condensation, or be thrown out in the precipitators. The dissolved salts with acid products of combustion would tend to form acids, the most volatile of which, hydriodic acid, in the dilution formed with the water of condensation from most samples, would have a negligible partial pressure (1, 5) even in the first collecting tube. If samples giving no water were being burned, it would be well to add a few cubic centimeters to the first collecting tube.

If we assume that the possible organic combinations of iodine are unstable under the conditions of combustion, it is evident that iodine itself is the next most probable source of loss under ideal operating conditions.

Of that part of the free iodine that is not held by basic materials after recombination, some will remain in solution in the condensed water vapor. Its slight solubility, however, will not allow us to depend on this factor for recovery, especially since the products of combustion of nitrogenous materials will insure the absence of iodides in solution. Aside from solution in water, we may expect iodine to be held as the condensed pure solid or more probably as a solid mixture with ice and other condensable combustion products. Concerning the state of these mixtures we know little except that the vapor pressure of iodine from them will likely be less than that of the pure solid. Occurring alone in the collecting tube (as it would seldom do with samples usually dealt with), iodine would be in its most fugitive condition. Of the behavior of pure elemental iodine we may speculate.

The approximate calculated vapor pressure (2, 6) of iodine in the temperature of the collecting tubes is of the order of 10^{-10} atmospheres. The loss in saturated emerging gas would be 0.1 or 0.2 γ of iodine per hundred liters. In a system utilizing its oxygen efficiently, this would mean a loss of less than 5 per cent on samples containing 100 parts of iodine per billion. The presence of almost any conceivable accompanying products of combustion would tend to decrease this loss.

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Determination of Copper Number of Paper

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AN INVESTIGATION into the service deterioration of the oil-impregnated paper insulation of 24,000-volt underground cable led to the use of the copper number test for following the changes which occurred in the paper. In a series of experiments in which oil and paper were subjected *in vacuo* to electric discharge (which had been shown to be one of the chief causes of service deterioration), it was found that an increase in the time or intensity of bombardment was accompanied by an increase in the copper number of the paper (12). The copper number was therefore used as an indication of the amount of deterioration.

Early tests in 1928 soon demonstrated the necessity of experimental work to modify one of the existing test methods for the determination of this factor so as to obtain a reliable test procedure for the requirements. The method finally adopted (7) has proved exceedingly satisfactory, and although essentially a standard method, the modifications are thought worthy of description as of general interest.

A copper number test, to be satisfactory for the purpose mentioned, must be rapid, sensitive, and capable of yielding results which are reproducible within reasonable limits on a sample not larger than 1.5 grams. In addition the apparatus required must not be expensive.

Early determinations were made by means of Schwalbe's method (13) and some of its modifications, but the results were unsatisfactory. The values obtained were erratic because of the instability of the Fehling solution during the boiling period, and because of the error due to adsorption by the paper of bivalent copper. Differences in paper samples subjected to different deteriorating treatments were not always brought out, probably because of the effect of caustic alkali in modifying the reducing properties of the cellulose (4).

In later work the method described by Braidy (2) and others (9), in which the Fehling solution is replaced by a sodium carbonate-bicarbonate solution, was used with more satisfactory results. As Clibbens and Geake point out (4), the method gives a low and constant blank, is sensitive to slight modifications of the cellulose, and is reproducible within reasonable limits.

Finally, the improved Braidy method as worked out by the Bureau of Standards and later published (3) was found, after minor modifications had been introduced, to satisfy the requirements completely. The Bureau of Standards specified a method of thoroughly disintegrating the paper without heating the fibers in order to obtain more accurate results. The Gault-Mukerji molybdophosphoric acid method (5) of determining the cuprous oxide was adopted. The size of the sample was reduced to 1.5 grams.

MODIFICATIONS OF OLD METHOD

The modifications of the Bureau of Standards method are as follows:

1. The shredder recommended by the Bureau of Standards was too large and costly for the type of work being carried out in these laboratories. A Hamilton-Beach malted milk mixer modified in the manner described by the Okonite Callender Cable Company (11) was found to meet the requirements.

The shredder is shown in Figure 1. The stirring motor was mounted on a telescoping shaft, A, so that it, together with the stirrer, could be raised or lowered to any desired height. A variable rheostat, B, was included to control the rate of stirring. A hotplate, C, was installed for heating the liquid during the shredding process. The original stirring shaft was replaced by a brass shaft, D, on which were mounted two shredding wheels 1.5 inches in diameter made from $\frac{1}{32}$ -inch sheet brass. Each wheel consisted of eight blades whose cutting edges were sharpened. The two wheels were

mounted so that the liquid was thrown upwards by the lower wheel and downwards by the upper wheel. The brass fingers, E, are important since they help to throw the fibers constantly into the shredding wheels. When used at high speed with a hot solution, the disintegration of the paper is complete after one minute. The short time involved eliminates the irregularities attendant upon long continued beating (8, 10).

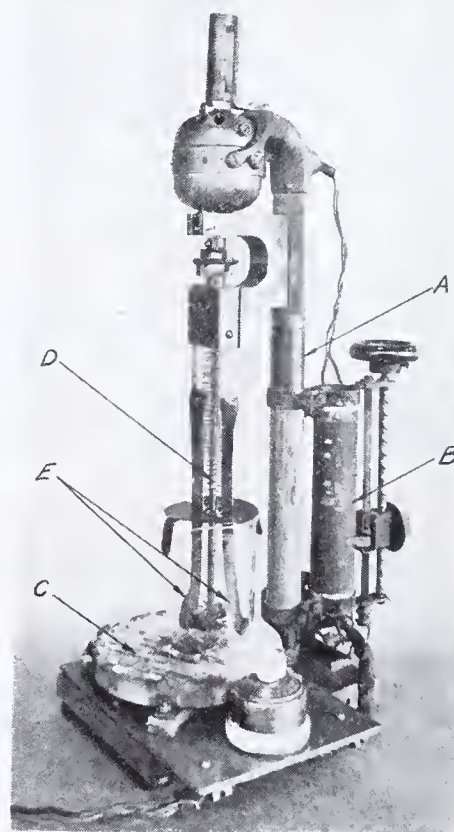


FIGURE 1. PAPER SHREDDER

2. Anhydrous sodium carbonate was used instead of the hydrated form because it was found that the latter form dehydrates and thus makes the concentration of the carbonate-bicarbonate solution uncertain.

3. The samples were weighed to the third decimal place to insure the accuracy of the second decimal place.

4. Coarse Jena filters suggested by Heyes (6) and Barthelmy (1) were substituted for filter paper on a Büchner funnel because, by so doing, thorough washing could be accom-

apparatus to within the limits of accuracy as defined by weighing. The fibers clinging to the beaker are rinsed free and the mixture is added to that in the Erlenmeyer flask. Five milliliters of the copper sulfate solution are added to the contents of the Erlenmeyer flask which is then swirled to mix the contents well, closed with a Bunsen valve, and submerged in a steam bath.

In actual practice, several samples are prepared up to the addition of the copper sulfate solution and a number of samples placed on the bath at one time.

At the end of 3 hours the flasks are removed from the bath and the contents filtered through Jena crucibles. When several samples are being run at once, all but those which can be filtered immediately are quickly cooled. The pulp is then washed with 75 to 100 ml. of 5 per cent sodium carbonate solution, and thoroughly washed with hot water. The washed pulp is transferred to a beaker containing 25 ml. of the molybdophosphoric acid solution and well macerated with a glass rod. Since particles of cuprous oxide clinging to the inside of the Erlenmeyer flasks are not removed when the flasks are rinsed into the crucibles, the flasks are rinsed with a portion of the molybdophosphoric acid solution, washed with water, and the solution added to the filtrate to be titrated. The mixture is allowed to stand for about 10 minutes and is then filtered through the same crucible as before. The filtrate is washed into a clean suction flask, and the solution transferred to a beaker and titrated with the standard potassium permanganate to a

faint pink color. A blank is run on the reagents alone in exactly the same manner as if they contained a paper sample. The value for the blank is subtracted from that of each sample.

Since the copper number is defined as the number of grams of metallic copper in the cuprous oxide reduced from the copper sulfate by 100 grams of sample, the following formula may be used:

$$\text{Copper number} = \frac{6.357 \times \text{ml. of KMnO}_4 \times N}{W}$$

where N is the normality of the potassium permanganate and W is the weight in grams of the sample. In order to correct for the moisture content of paper, it is necessary either to make the moisture determination on a separate sample, or to remove the moisture under conditions which do not alter the paper in such a way as to effect changes in the copper number. Since the specimens used were so small as to preclude the use of the former method, it was desirable to use the latter. By drying the sample (100° to 110° C.) 2 hours in a stream of dry nitrogen, the moisture is removed to the point where any further change in weight does not affect the accuracy of the result. However, even when care is taken to displace the air surrounding the samples before starting the drying, the mild heat treatment raises the copper number slightly more than the probable error of the determinations (Figure 2). This is shown by the following table:

COPPER NO. OF PAPER DRIED 2 HOURS IN N	COPPER NO. OF UNDRIED PAPER COR. FOR MOISTURE
1.02	1.01
1.02	1.01
1.03	1.00
1.03	1.00

Unless care is taken to displace the air before heating is started, the difference is greater. In all cases where possible

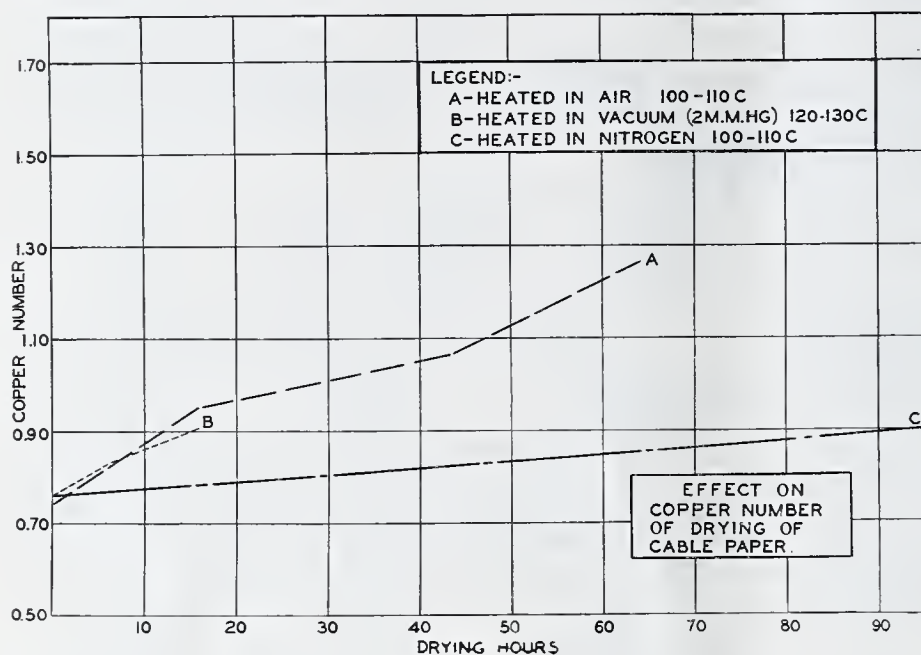


FIGURE 2

plished with less water, thus increasing the sharpness of the end point in the titration. The elimination of the filter paper in this manipulation decreased the value of the blank determination which is always run in conjunction with the samples. The reagents used in this determination are (3):

Copper sulfate solution: 100 grams $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per liter of water
Carbonate-bicarbonate solution: 50 grams NaHCO_3 and 132 grams anhydrous Na_2CO_3 per liter of water
Molybdophosphoric acid solution: 100 grams sodium molybdate (43% by wt. Mo) and 75 ml. 83% H_3PO_4 added to a solution of 275 ml. H_2SO_4 (sp. gr. 1.86) and 1750 ml. water
Sodium carbonate solution: 5% Na_2CO_3
Potassium permanganate solution: 0.02 N

DETAILED PROCEDURE

Forty-five milliliters of the carbonate-bicarbonate solution are placed in a tall form 300-ml. beaker and the beaker set on the hotplate, C , of the shredding apparatus. A 1.5-gram sample of the paper, weighed to the third decimal place, is torn into pieces about one quarter of a square inch. At the first sign of steam rising from the solution on the hotplate (90° to 95° C.), the heater is turned off and the bits of paper making up the sample are transferred to the beaker. The shredding wheel is then lowered into the mixture and the machine run at full speed for exactly one minute. During the shredding the beaker is pushed off center to facilitate cutting the pieces of paper which might otherwise escape the process. At the end of one minute of shredding the wheel is lifted above the surface of the mixture, but not above the top of the beaker, and the motor stopped. The contents of the beaker are then transferred to a 125-ml. Erlenmeyer flask. (A funnel with the stem cut off facilitates this step.)

Fifty milliliters of the cold carbonate-bicarbonate solution are then added to the beaker and the motor run as before. This treatment removes the fibers clinging to the grinding

it seems advisable, therefore, to determine the moisture content of the paper on separate samples.

It frequently has been pointed out that the empirical nature of the copper number determination renders it highly dependent on the details of the experimental procedure. The temperature during the digestion period (2, 4, 14), the time of digestion (2, 9), and the concentration of the alkaline solution (1) must be kept constant if strictly comparable results are to be obtained.

The reproducibility of the results can be illustrated from the following:

Ten copper number determinations made on a given cable paper averaged 0.96. The highest value was 0.98 and the lowest 0.95. However, abnormal values, both high and low, are occasionally obtained from the same sheet of cable paper. Whether these are due to actual differences in the paper or to errors in manipulation is not known. Determinations made on a large number of samples of cable paper indicate that it is advisable to interpret the value of a single determination plus or minus about 2.5 per cent.

ACKNOWLEDGMENT

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Impurities in White Sugars

VI. Direct Determination of Chlorides

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CHLORIDES in sugarhouse products are often determined in the lixiviated ash, although Browne and Gamble (1) have shown that chlorine is lost during the charring preparatory to the lixiviation and recommend the direct gravimetric determination of chlorides in these products. With high concentrations of sucrose and low content of chlorides, however, the sucrose exerts a dispersing action on the precipitated silver chloride, so that collection of the silver chloride upon a filter is very difficult and often impossible. To overcome this difficulty, Budlovsky (2) has proposed a method of coagulating the silver chloride formed in sucrose solutions by precipitating ferric phosphate in the solution containing the suspended silver chloride. The precipitate of silver chloride and ferric phosphate is then treated in a special distilling apparatus with sulfuric acid. The hydrogen chloride liberated is distilled into water and determined by a nephelometric titration with mercuric nitrate.

TABLE I. DETERMINATION OF CHLORIDES IN PRESENCE OF SUCROSE

Cl ⁻ ADDED Mg.	Cl ⁻ FOUND IN ABSENCE OF SUCROSE Mg.	Cl ⁻ FOUND IN PRESENCE OF 100 GRAMS OF SUCROSE Mg.
0.35	0.21	0.21
0.71	0.74	0.82
1.42	1.49	1.42
2.13	2.06	2.20
2.84	2.91	2.84
3.55	3.48	3.62
4.26	4.11	4.33
4.96	5.11	5.25
5.67	5.75	5.75
6.38	6.31	6.45
7.09	7.09	6.81

The proportion of chlorides present in white consumption sugars is so small that gravimetric determination is impractical. The direct volumetric determination of chlorides in white sugars has not been reported, so far as the authors are aware. The experiments reported in Table I show that Mohr's method (3) of titration of chlorides with silver nitrate and potassium chromate as indicator may be success-

fully applied. Although sucrose prevents the coagulation of silver chloride, there is no indication that it interferes with the removal of chloride ions by the silver ions.

One hundred grams of sugar were dissolved in about 150 cc. of distilled water, and about 0.5 cc. of saturated potassium chromate solution was added. The solution was titrated with 0.02 N silver nitrate solution as usual for the volumetric titration of chlorides.

The content of chlorides in various grades of commercial white sugars is shown in Table II.

TABLE II. CHLORIDE IN COMMERCIAL WHITE SUGARS

SUGAR	Cl ⁻ P. p. m.	SUGAR	Cl ⁻ P. p. m.
a	7.8	k	33.3
b	1.4	l	27.7
c	40.4	m	0.0
d	17.7	n	5.0
e	33.3	o	22.7
f	0.7	p	39.0
g	31.9	q	44.0
h	14.2	r	31.9
i	16.3	s	20.6
j	2.1	t	10.6

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- (1) Browne and Gamble, *Facts About Sugar*, 17, 552 (1923).
- (2) Budlovsky, *Z. Zuckerind. czechoslovak. Rep.*, 52, 421 (1927-28).
- (3) Mohr, *Ann.*, 97, 335 (1856).

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CORRECTION. In the article on "Apparatus for Reactions in Liquid Phase at Elevated Temperatures and Pressures" [*IND. ENG. CHEM., Anal. Ed.*, 4, 342 (1932)], the length of the tubing for the steel spiral referred to in the thirteenth line from the bottom of the first column, page 343, should have been given as 4.3 meters, or 14 feet.

HOMER ADKINS

Improved McLeod Gage and Manometer

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IN SPITE of the numerous improvements made in the McLeod gage since the original devised by McLeod (3), it still suffers from certain defects. In order to overcome some of these, there has been devised in this laboratory the modification shown in Figures 3 and 4.

A better appreciation of this device may be obtained, perhaps, if the original McLeod gage, as shown in Figure 1, be considered first. In this device the apparatus whose pressure is to be measured is connected to the body of the McLeod gage through the capillary between *B* and *F*. When equilibrium has been attained between the McLeod gage and the apparatus, the mercury reservoir, *R*, is slowly raised, imprisoning above the cut-off, *C*, the gas of volume V_1 and compressing it into the calibrated capillary, *OT*. Simultaneously, the mercury will rise in the capillary *BF*. This instrument may then be used in either of two ways: First, the mercury may be allowed to rise in capillary *OT* exactly to *O*, and the difference in height, *H*, between *O* and the top

useful for low pressures, the mercury is adjusted so that the height of the column in the capillary *BF* (Figures 1 and 2) or *OF* (Figures 3 and 4) coincides exactly with the height of *T*, the mercury in the capillary *OT* being at some height, *L*. If we let *H* represent the difference in height in mm. between *L* and *T*, and if *v* represents the volume of the capillary *OT* per mm. of height, then the equation becomes

$$P = H \times \frac{Hv}{V_1} \quad (2)$$

However, in neither of these formulas is the fact recognized that pressure *H* should be corrected for pressure *P* being measured. Formula 1 then becomes

$$P = (H + P) \frac{V_2}{V_1}, \text{ whence } P = H \frac{V_2}{V_1 - V_2} \quad (3)$$

and Formula 2 becomes

$$P = (H + P) \frac{Hv}{V_1}, \text{ whence } P = \frac{H^2v}{V_1 - Hv} \quad (4)$$

In measuring low pressures this correction may be omitted. However, in the use of the vacuumeter to measure pressures of the order of several millimeters, it should be included. The type of vacuumeter shown in Figure 1 is usually used for measuring relatively low vacuums, whereas that in Figure 2 is more commonly used for measuring high vacuums.

In Figure 2 the diffusion of the gas between the vacuumeter and the apparatus has been greatly facilitated by using a tube of large bore and making the capillary a by-pass. However, this type of apparatus can only be used according to the second method.

If one desires, therefore, to measure a considerable range of low pressure, it is necessary to have two vacuumeters, one such as Figure 1 and the other such as Figure 2. This has been obviated in our design as shown in Figure 3. A tube of large bore, *B*, connects the vacuumeter and the apparatus whose pressure is to be measured. At a distance of about 85 cm. below the constriction, *C*, the side tube, *EOF*, is attached. The upper part of the tube is made of capillary tubing of the same piece as was used in the body of the vacuumeter. Thus there is no capillary error due to differences in diameter. Above the capillary tube at *F* there is a short space of 7-mm. tubing surmounted by another capillary tube, which is bent downward and again upward at the overflow well, *W*. The distance from the top of the capillary tube to *W* should be about 760 mm. The total length of the capillary from *O* to *F* should be about 1 meter.

CALIBRATION AND PREPARATION OF GAGE

The volume *v* of the capillary tube in cubic millimeters per mm. of length should be determined before attaching the capillary to the body of the tube. The capillary should be tested first for uniformity by placing in a suitable length of the capillary tubing a drop of mercury and measuring the length of this drop in different positions in the capillary. In a capillary of uniform bore the length of the drop of mercury will be constant. To calibrate it the capillary tube is almost filled with pure mercury. The length of this mercury column is measured, the temperature noted, and the mercury run out and weighed. The capillary tube is then sealed on to the gage body and sealed off at the top, *T*, with



FIGURE 1

FIGURE 2

of the column of mercury in the capillary side tube, *BF*, noted. Then it is obvious that, assuming the perfect gas laws, the true pressure, *P*, in the system connected to the gage is

$$P = H \times \frac{V_2}{V_1} \quad (1)$$

where V_2 is the volume of the gas in the capillary *OT*.

In the other method of operation, which is particularly

as blunt an end inside as possible. The gage is then clamped in inverted position and filled with pure mercury up to the constriction, *C*, the temperature noted, and the mercury removed and weighed. If the temperature at which both

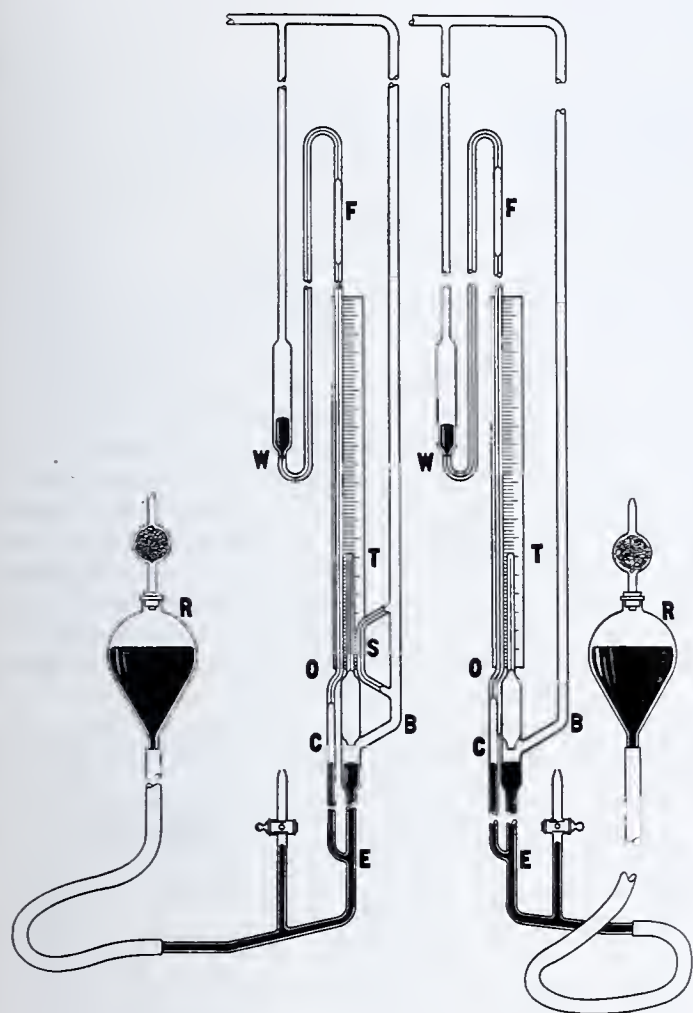


FIGURE 4

FIGURE 3

the capillary and whole gage are filled are the same, it is unnecessary to calculate the true volumes, and the relative weights may be used instead to get the constant v/V_1 for the gage.

In operation the vacuumeter is first carefully cleaned and thoroughly dried by passing dry air through it for a number of days, or better, by repeated rinsings with dry air followed by evacuations. Then the reservoir, *R*, is filled with pure mercury and kept at such a low level that when a vacuum is applied to the gage the mercury will slowly rise in the lower tube. When a satisfactory vacuum has been obtained, the reservoir, *R*, is raised until the mercury overflows into *W*. The reservoir is then lowered at once as low as possible, the column of mercury breaks at *F*, and opportunity is given for adsorbed gases to escape from the walls of *OF*. After a few minutes, *R* is again raised, thus driving over any minute amounts of gas which may have escaped from the walls of *OF*. The instrument should then be allowed to stand with reservoir *R* as low as possible, and at daily intervals *R* should be raised to drive over any gas while the space above *W* is evacuated to expand the bubble and prevent its lying down in the capillary. When no evidence is seen of a bubble of gas being carried over into *W*, it may be assumed that the space in *OF* is completely evacuated, and the gage is ready for use.

This instrument may be used over a wide range of pressures. One made in this laboratory is sensitive over the range from 760 to 0.00001 mm., although according to Gaede (1) accurate measurements below 0.0001 mm. can be made

only on hydrogen or nitrogen, or a similar inert noncondensable gas. Oxygen at these low pressures tends to smut the mercury, probably because of the formation of ozone by the activation of the oxygen by the electrical discharge produced by the moving mercury. This smut deposits as a film in the capillary, obviously introducing errors. From pressures between 17 and 0.1 mm. (gage *A* in Table I), the procedure is as follows: The reservoir is raised slowly until mercury in the body of the tube has risen to the etched mark, *O*, in the capillary, *OT*. The difference in height, *H*, between *O* and the column of mercury in *OF* is noted. Whence

$$P = H \times \frac{V_2}{V_1}$$

where V_2 represents the volume of the gas compressed in the capillary above *O*. Since there is no pressure above the side capillary, *OF*, no correction for this is necessary as was the case in the original design shown in Figure 1 (see Equation 3).

TABLE I. DIMENSIONS AND CONSTANTS OF TWO TYPICAL NEW TYPE GAGES

	A	B
Inner diam. of capillary <i>OT</i> , mm.	1.75	1.07
Length of capillary <i>OT</i> , mm.	260	320
Inner diam. of body of gage, mm.	16	28
Approx. length of body of gage, mm.	90	150
Volume v of capillary, cu. mm. per mm.	1.030	0.9052
Volume V_1 of whole gage, cu. mm.	15,260	77,720
Gage constant V_2/V_1 (Equation 1)	1/56.98	1/268.3
Gage constant v/V_1 (Equation 2)	1/14,815	1/85,856
OPERATING GAGE ACCORDING TO EQUATION 1		
If $P = 1$ mm., H	=	56.98 mm. 268.3 mm.
3 mm., H	=	170.94 mm. 804.9 mm.
10 mm., H	=	569.8 mm. Beyond range
17 mm., H	=	968.7 mm. Beyond range
OPERATING GAGE ACCORDING TO EQUATION 2		
If $P = 1.00$ mm., H	=	122.0 mm. 293.0 mm.
0.01 mm., H	=	12.2 mm. 29.3 mm.
0.0001 mm., H	=	1.22 mm. 2.93 mm.
0.00001 mm., H	=	0.39 mm. 0.93 mm.

If low pressures are to be measured, the mercury is allowed to rise in *OF* to the same level, *T*, as the top of the inside of the capillary on the body of the gage. The difference in level, *H*, between *T* and the mercury column of the capillary on the body of the gage is noted. Then the true pressure

$$P = H^2 \times \frac{v}{V_1}$$

where V_1 equals the total volume in cubic millimeters of the gage above the constriction *C*, and v equals the volume in cubic millimeters per mm. of length of the capillary on the body of the gage. Again there is no correction for the pressure in the external system (see Equation 4).

To measure higher pressures—that is, to use the gage as a manometer—the design shown in Figure 4 equipped with capillary side tube *S* is required. The reservoir is adjusted so that the mercury level in *S* is at *O* and the difference in levels between the mercury in *OF* and in *S* is the pressure of the outside system being measured.

In building a gage of this new type it is important to have the proper ratio between the total volume of the gage, V_1 , and the total volume of the capillary. To avoid sticking of the mercury in the capillary, its inner diameter should be greater than 0.5 mm. Although for very low pressures the body of the gage may be even as large as 500 cc., for most uses in the laboratory it is best to have this volume around 50 cc. For the convenience of those wishing to build one of these new gages, there is described in Table I the complete dimensions and pressure data of two gages of this type of different range actually in use in this laboratory.

To minimize smutting of the mercury, these gages may be

operated by vacuum-pressure control arrangements, such as that devised by Gaede (1) or the General Electric Company modification (2), provided the reservoir is connected to an air-pressure line to force the mercury over the top when evacuating capillary OF.

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- (2) Kaye, "High Vacua," p. 128, Longmans, 1927.
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Determination of Silicon in Steels

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ALTHOUGH it is a well-known fact that in the determination of silica in silicates accurate results can be obtained only when several dehydrations are made, it has long been the practice of steel chemists to consider the amount of silica left in iron solutions after a single dehydration as being negligible. However, in the last few years there have been several attempts to show that for accurate work more than one dehydration is necessary, especially if the silicon content is high. For example, Pinsel (6) claims that when cast irons are analyzed by the nitro-sulfuric acid method the results are low, and that for umpire work several evaporations cannot be avoided.

Stadeler (7), while studying the relative advantages of the various methods for silicon, had three steels of different silicon contents analyzed by twelve laboratories, employing five different methods. All of these laboratories found silicon in the filtrate after a single dehydration. The twelve laboratories varied widely in the percentages of silicon recovered in a second dehydration, averaging 0.01, 0.02, and 0.14 per cent on an 0.08, a 0.3, and a 4 per cent silicon steel, respectively. However, the results for the first evaporation differed so greatly as to throw doubt on any conclusion as to the amount of silicon recoverable in a second dehydration. Wolf and Heilingötter (10) analyzed a sample of high-silicon steel by five methods, making four dehydrations by each method. For their standardization procedure they chose a nitro-sulfuric acid method, which yielded an average of 4.004 per cent of silicon in the first dehydration, 0.068 in the second, 0.039 in the third, and 0.019 in the fourth. The total, 4.130 per cent, was considered to be the silicon content of the steel. Four dehydrations by each of the other methods gave values ranging from 4.078 to 4.116 per cent, results which were from 0.014 to 0.062 per cent lower than those obtained by the nitro-sulfuric acid method.

In the analysis of Bureau of Standards standard samples of steel it has been the practice to make two dehydrations by the sulfuric acid method. The results obtained on a number of these standards are given in Table I.

TABLE I. SILICON OBTAINED BY SULFURIC ACID METHOD

TYPE OF STEEL	WT. OF SAMPLE Grams	Si OBTAINED IN 1ST DE- HYDRATION	Si OBTAINED IN 2ND DE- HYDRATION	TOTAL SILICON %
		%	%	
0.4 Carbon, B. O. H.	10	0.017	0.001	0.018
0.1 Carbon, Bessemer	10	0.020	0.001	0.021
0.4 Carbon, Bessemer	10	0.062	0.002	0.064
0.6 Carbon, A. O. H.	10	0.105	0.002	0.107
Medium manganese	10	0.192	0.003	0.195
Chrome-nickel	10	0.213	0.007	0.220
0.6 Carbon, A. O. H.	5	0.276	0.004	0.280
1.0 Carbon, A. O. H.	10	0.381	0.007	0.388
Acid electric	10	0.434	0.007	0.441

The silicon content of three typical steels has been determined by solution, dehydration, and recovery of the dissolved silicon by volatilization of the iron with hydrochloric acid gas. The percentage of silicon obtained by a single dehydration with five common methods for the determination of silicon is compared with the values for total silicon. An umpire method for silicon in very low-silicon irons is also described.

Table II shows the results obtained by thirteen analysts on a standard steel. Column 3 shows values they reported on first analyzing the steel, and column 5 the results they obtained when the steel was returned to them for reanalysis with a request that they make two dehydrations for silicon. These data indicate that if the silicon content of a steel is

as high as 0.4 per cent, a second dehydration is necessary for accurate work.

TABLE II. SILICON IN STANDARD STEEL REPORTED BY THIRTEEN ANALYSTS

ANALYST	—FIRST ANALYSIS—		—SECOND ANALYSIS—	
	No. of de- hydrations	Values reported %	No. of de- hydrations	Values reported %
1	2	0.441 ^a
2	1	0.434 ^a
3	1	0.388 ^a	2	0.438 ^a
4	1	0.412 ^a	2	0.440 ^a
5	1	0.409 ^b	2	0.441 ^a
6	1	0.408 ^b	2	0.436 ^a
7	1	0.420 ^b	2	0.446 ^a
8	1	0.407 ^d	2	0.441 ^a
9	1	0.422	2	0.439 ^a
10	1	0.417	...	0.440
11	1	0.427 ^c	2	0.451 ^c
12	1	0.422 ^d	1	0.434 ^b
13	1	0.435 ^e
		Av. 0.419		Av. 0.441

^a Sulfuric acid method.

^b Nitro-sulfuric acid method.

^c Nitro-hydrochloric acid method.

^d Hydrochloric acid method.

^e Perchloric acid method.

DETERMINATION OF MOST PROBABLE VALUES FOR SILICON

In view of the uncertainty concerning the amount of silicon remaining in solution after dehydration by the usual procedures, it was decided to attempt to determine the true silicon content of three typical steels and then to compare these values with those obtained when the usual procedures were applied. Steels representing the ranges of silicon usually encountered in steel laboratories were selected for this work. The samples were in the form of fine chips as prepared for Bureau of Standards standard samples (4). For convenience they will be referred to as steels A, B, and C throughout this paper. Their silicon contents were approximately 4.7, 0.4, and 0.1 per cent.

The other constituents were as follows:

STEEL	TYPE	C %	Mn %	P %	S %	Ni %	Cr %	V %
A	Unknown	0.064	0.10	0.010	0.024	0.242	0.178	0.007
B	Acid electric	0.258	0.748	0.036	0.048	0.030	0.166	0.008
C	A. O. H.	0.574	0.630	0.062	0.030	0.161	0.166	0.008

In the analysis of silicate materials, such as rocks, it is usually assumed that the silica which escapes the dehydrating

treatment will be found in the ammonia precipitate, and that it can be recovered by igniting this precipitate and volatilizing the silica in the usual manner with hydrofluoric acid. As it would have been inconvenient to filter, ignite, and weigh the oxide which would be obtained if 5 grams of steel were precipitated with ammonium hydroxide, attempts were made to reduce the iron completely to the ferrous condition, then to add 75 to 150 mg. of ferric iron, and finally to precipitate the added iron by adding dilute ammonium hydroxide until a permanent precipitate was obtained, boiling for a few minutes, and filtering. The precipitate should then contain the silicon which could be recovered as already indicated. It was found, however, that although the amount of iron oxide precipitated by this procedure was fairly constant, the silicon recovery was never quantitative when the procedure was applied to iron solutions containing known amounts of dissolved silicon.

Volatilization of the iron as ferric chloride by means of a current of dry hydrochloric acid gas seemed, next to the ammonia separation, to offer the most promise as a means of determining the dissolved silicon. This method was first described by Boussingault (1) and has since been used for a member of the separations, such as iron from alumina (2) and tungsten from silica (3).

For the exact determination of silicon in these steels, it was decided first to dehydrate with sulfuric acid and then to recover the dissolved silicon by volatilizing the iron as ferric chloride by means of hydrochloric acid gas.

The following procedure was employed: One or more dehydrations, according to the procedure given below, were made in one-liter platinum dishes provided with platinum covers. The filtrate from the last dehydration was evaporated to dryness in the covered platinum dish, the sulfuric acid expelled by gentle ignition, and the residue finally heated to redness. The dish was cooled, and the residue transferred to a small platinum boat. This was then placed in a Pyrex or silica tube in a split-type electric combustion furnace, heated to 400° to 700° C., and a slow current of dry hydrochloric acid gas passed through the tube. The hydrochloric acid gas was generated by dropping sulfuric acid upon heated ammonium chloride and dried by bubbling through sulfuric acid.¹ The residue adhering to the dish was treated with a few milliliters of hydrochloric acid, transferred to a platinum crucible, and the solution evaporated to dryness. When most of the iron in the boat had been volatilized, the residue was carefully brushed into the crucible containing the residue from the dish. The contents of the crucible were treated with a few drops of dilute sulfuric acid, which was then driven off by heating the crucible on a radiator. The residue was next ignited in a muffle at 1050° to 1100° C. to constant weight, treated with 10 ml. of hydrofluoric acid and a few drops of dilute sulfuric acid (1 to 3), and the amount of silica determined by evaporation to dryness on a radiator, igniting, and weighing. The weight of the nonvolatile residues averaged about 0.15 gram.

The first few times the volatilization procedure was used, the initial dehydration was made by the perchloric acid method because it was believed that residues from perchloric acid solutions could be converted to oxides more readily than those from sulfuric acid solutions. Later experiments with sulfuric acid showed that the residue from a sulfate solution was in a better condition to be attacked with hydrogen chloride than residues from perchloric acid solu-

tions. When perchloric acid was used, the procedure given under "Perchloric Acid Method" below was followed. The results obtained for total silicon by both methods are listed in Table III. The values given were corrected by complete blank determinations.

TABLE III. SILICON OBTAINED BY SULFURIC ACID AND PERCHLORIC ACID METHODS AND RECOVERY OF DISSOLVED SILICON

SILICON OBTAINED						
WT. OF SAMPLE	METHOD	1st dehy-	2nd dehy-	3rd dehy-	After HCl	Total
Grams		dration	dration	dration	volatili-	
		%	%	%	%	%
STEEL A						
2.336	H ₂ SO ₄	4.634 ^a	0.036	0.006	0.007	4.683
2.336	H ₂ SO ₄	4.666	0.026	0.006	0.008	4.706
2.336	H ₂ SO ₄	4.646	0.036	0.006	0.007	4.695
2.336	H ₂ SO ₄	4.638	0.038	0.006	0.008	4.690
2.336	H ₂ SO ₄	4.678	0.024	4.702
2.336	HClO ₄	4.672	0.022	4.694
2.336	HClO ₄	4.678	0.020	4.698
2.336	HClO ₄	4.678	0.022	4.700
						Av. 4.696
STEEL B						
5.00	H ₂ SO ₄	0.435	0.005	0.005	0.006	0.451
5.00	H ₂ SO ₄	0.435	0.005	0.005	0.008	0.453
5.00	H ₂ SO ₄	0.435	0.016	0.451
5.00	H ₂ SO ₄	0.438	0.009	0.447
5.00	HClO ₄	0.437	0.012	0.449
5.00	HClO ₄	0.438	0.010	0.448
						Av. 0.450
STEEL C						
5.00	HClO ₄	0.106	0.008	0.114
5.00	HClO ₄	0.105	0.006	0.111
5.00	HClO ₄	0.107	0.004	0.111
5.00	H ₂ SO ₄	0.107	0.002	0.001
5.00	H ₂ SO ₄	0.106	0.001	0.002
5.00	H ₂ SO ₄	0.104	0.003	0.003
						Av. 0.112

^a Results obtained in single determinations are obviously not accurate to third decimal place for high-silicon steels, but are so given because averages are computed.

The average values shown in Table III are believed to be very close to the true silicon contents of the steels. These may be considered to be as follows: steel A, 4.696 per cent \pm 0.005; steel B, 0.450 per cent \pm 0.002; steel C, 0.112 per cent \pm 0.002.

Subsequent work on the determination of silicon by dissolving the steel in nitric acid, evaporating, igniting, and volatilizing the iron as above, indicated small losses of silicon in the case of steels A and C when this procedure was followed. Steel B gave slightly higher results. The results in the case of steels B and C are practically within the limits of error of the volatilization method, whereas the error in the case of steel A, amounting to an average of 1.5 mg. of silica, is probably due to mechanical loss in transferring the silica from the boat to the crucible. Results for the direct determination are listed in Table IV.

TABLE IV. SILICON OBTAINED BY DIRECT METHOD

WT. OF SAMPLE Grams	SILICON	
	Found %	Present %
STEEL A		
2.336	4.670	
	4.668	
2.336	4.663	
	4.665	
	Av. 4.667	4.696 \pm 0.005
STEEL B		
2.336	0.452	
	0.454	
5.000	0.456	
	0.445	
	Av. 0.452	0.450 \pm 0.002
STEEL C		
5.00	0.107	
	0.108	
	0.109	
	Av. 0.108	0.112 \pm 0.002

SILICON RECOVERED BY SINGLE DEHYDRATION

As repeated evaporations are laborious and the hydrochloric acid volatilization method time-consuming, it was

¹ The hydrogen chloride generator consisted of a 6-liter Florence flask, fitted with a Kjeldahl bulb and a dropping funnel, and heated with a Bunsen burner. Technical sulfuric acid was allowed to drop slowly from the funnel on heated ammonium chloride. The hydrogen chloride generated, together with some water vapor, passed through the spray trap into a wash bottle containing concentrated technical sulfuric acid, and then into the furnace. The sulfuric acid was renewed frequently.

thought desirable to find out what kind of results could be expected if single dehydrations were made by the ordinary methods for the determination of silicon in steels. In an attempt to eliminate errors other than those inherent in the methods, all evaporations except those with hydrochloric acid were made in liter platinum dishes provided with platinum covers, and all ignitions were made in an electric muffle controlled with a pyrometer. Blanks were run on all the reagents and any silicon found deducted.

The following methods were studied (5):

SULFURIC ACID METHOD. The sulfuric acid method as used at the Bureau of Standards is as follows: Dissolve the sample, 4.672 grams of steels containing less than 0.5 and 2.336 grams of steels containing over 0.5 per cent silicon, in 100 ml. of sulfuric acid (1 to 4). Evaporate the solution, taking care to avoid spattering, until copious fumes of sulfuric acid are evolved. Continue the fuming for 2 to 4 minutes, but no longer lest insoluble sulfates be formed. Cool somewhat and add 125 ml. of warm water (40° to 50° C.) at one stroke. Stir until salts are in solution, heating lightly if necessary, but never to boiling. Immediately filter through rapid paper such as S & S No. 589 Black Band (tighter paper for low-silicon steels), scrubbing the dish thoroughly with a rubber "policeman." Wash the paper several times with dilute hydrochloric acid (5 to 95) to remove most of the iron salts, and then several times with hot water. Transfer the paper and contents to a platinum crucible, char the paper at a low temperature, preferably in an electric muffle, and finally ignite to constant weight at 1050° to 1150° C. Cool in a desiccator and weigh. Moisten the silica with a few drops of dilute sulfuric acid (1 to 3), add an excess of hydrofluoric acid (3 to 5 ml.), evaporate to dryness in an air bath, ignite, and weigh. This method gave the results listed in column 3 of Table V.

TABLE V. SILICON OBTAINED IN SINGLE EVAPORATIONS

WT. OF SAMPLE Grams	SILICON PRESENT %	—SILICON BY FOLLOWING METHODS:—				
		H ₂ SO ₄ %	HNO ₃ - H ₂ SO ₄ %	HClO ₄ %	HCl %	HCl- NH ₄ Cl %
STEEL A						
2.336	4.696 ± 0.005	4.634	4.612	4.672	4.628	4.638
		4.646	4.594	4.678	4.628	4.642
		4.678	4.598	4.658	4.638	4.642
		4.660	4.570	4.670	4.638	4.640
		4.664	4.612	4.664	4.628	4.642
		4.650	4.610	4.678	4.628	4.634
		4.666		4.656		
		4.666		4.672		
		4.638		4.664		
		4.678				
		4.660				
		4.660				
		4.672				
		4.666				
	Av. 4.660	4.599	4.668	4.631	4.640	
STEEL B						
4.672	0.450 ± 0.002	0.435	0.427	0.437	0.429	0.430
		0.435	0.433	0.435	0.427	0.429
		0.435	0.432	0.432	0.427	0.425
		0.433		0.438		
		0.435		0.436		
		0.438		0.435		
			Av. 0.435	0.431	0.436	0.428
STEEL C						
4.672	0.112 ± 0.002	0.107	0.105	0.105	0.102	0.101
		0.104	0.105	0.105	0.100	0.106
		0.104	0.105	0.105	0.103	0.103
		0.107		0.106	0.103	0.102
		0.104		0.106	0.108	0.104
		0.106		0.106		
		0.105		0.107		
		0.105		0.105		
		0.106				
			Av. 0.105	0.105	0.106	0.103

NITRO-SULFURIC ACID METHOD. Dissolve the sample, 4.672 grams of steels containing less than 0.5 per cent of silicon and 2.336 grams of steels containing over 0.5 per cent of silicon, in 80 ml. of nitro-sulfuric acid mixture (2000 ml. of sulfuric acid, sp. gr. 1.84, 1500 ml. of nitric acid, sp. gr. 1.42, and 5500 ml. of water). Evaporate until copious fumes of sulfuric acid are evolved. Cool somewhat and cautiously add to the warm residue 5 ml. of hydrochloric acid (sp. gr. 1.19) and 125 ml. of warm water (40° to 50° C.). Stir and warm until salts are in solution, but do not heat strongly unless the salts cannot be otherwise dissolved. The heating should not require more than 5 minutes. Immediately filter and proceed as above.

This method gave the results shown in column 4 of Table V.

PERCHLORIC ACID METHOD. The perchloric acid method (9) has rapidly come into favor with the increasing use of steels containing considerable amounts of chromium and nickel, which yield difficultly soluble sulfates in the sulfuric acid methods. Perchloric acid forms salts with these metals that are very readily soluble. The following method was used:

Dissolve the sample, 4.672 grams of steels containing less than 0.5 per cent and 2.336 grams of steels containing more than 0.5 per cent silicon, in 60 or 40 ml., respectively, of dilute nitric acid (1 to 1). When solution is complete, add 60 or 40 ml. of perchloric acid (60 to 70 per cent), depending on the weight of sample taken. Evaporate to fumes of perchloric acid, cover the dish, and continue heating at such a rate that the solution boils and perchloric acid refluxes on the sides of the dish for 15 to 20 minutes. Cool somewhat, add 125 ml. of hot water at one stroke, and proceed as above, with the exception that the larger residues from high-silicon steels must be washed well with hydrochloric acid (1 to 1) or they will decrepitate badly when ignited.

This method gave the results shown in column 5 of Table V.

HYDROCHLORIC ACID METHOD. Dissolve the sample, 4.672 grams of steels containing less than 0.5 per cent and 2.336 grams of steels containing over 0.5 per cent of silicon, in 60 ml. of hydrochloric acid (1 to 1) in a 400-ml. beaker, evaporate to dryness, and bake for one hour at 105° to 120° C. Baking at temperatures higher than 120° C. will produce residues which dissolve with difficulty. Drench the hot residue with 15 ml. of hydrochloric acid (sp. gr. 1.19), stir for about one minute, add 125 ml. of hot water, continue the stirring until salts are in solution, and proceed as in the sulfuric acid method.

This method gave the results shown in column 6 of Table V.

HYDROCHLORIC ACID-AMMONIUM CHLORIDE METHOD. Proceed exactly as in the hydrochloric acid method but add 5 grams of ammonium chloride before evaporating the solution to dryness. The addition of ammonium chloride causes the baked residue to be more readily soluble.

This method gave the results shown in column 7 of Table V.

The difference in the results obtained by the sulfuric acid and perchloric acid methods in the case of steel A is of about the same order of magnitude as the limits of error of the two methods. The other three methods gave results which were definitely lower, and hence are not so satisfactory with single dehydrations for high-silicon steels. For low-silicon steels such as steels B and C, all five methods give acceptable results, although those obtained by dehydration with hydrochloric acid and hydrochloric acid and ammonium chloride are lower than the other three.

TABLE VI. SILICON OBTAINED IN BUREAU OF STANDARDS STANDARD SAMPLE OF INGOT IRON No. 55

METHOD	RUN	WT. OF SAMPLE Grams	SILICA FOUND Gram	SILICON FOUND %
Single dehydration with H ₂ SO ₄	1	20	0.0001	0.0002
	2	20	0.0001	0.0002
	3	10	0.0001	0.0005 ^a
	4	10	0.0001	0.0005 ^a
Sample dissolved in H ₂ SO ₄ , evaporated, residue ignited, iron volatilized with HCl, etc.	5	10	0.0003	0.0014
	6	10	0.0005	0.0023
	7	20	0.0009	0.0021
	8	20	0.0010 ^b	0.0023

^a Analysis made by C. P. Larrabee in 1923.

^b Hydrochloric acid residue fused with Na₂CO₃, melt dissolved in sulfuric acid, solution fumed, and silica determined. Soluble silica in filtrate, amounting to 0.2 mg., was estimated colorimetrically by ammonium molybdate method of Thayer (8).

DETERMINATION OF SILICON IN IRONS AND STEELS CONTAINING VERY LITTLE SILICON

Although volatilizing the iron as ferric chloride is not a suitable method for routine determinations of silicon in steels, it is particularly valuable for the accurate determination of the very small amounts of silicon in materials such as ingot iron. The silicon content of these materials is often so low that the results obtained by the usual dehydration with acid are of about the same order of magnitude as the blank. Determinations 1 to 4 of Table VI were made by dehydrating 10- to 20-gram samples of the Bureau of Stand-

ards Ingot Iron No. 55 with sulfuric acid, as described in the sulfuric acid method above. Determinations 5 to 8 were made by dissolving 10- to 20-gram samples of the iron in sulfuric acid, evaporating, igniting, and volatilizing with hydrochloric acid. Blanks were determined on all reagents used, and any silica found was subtracted. In no case was a blank of more than 0.2 mg. of silica obtained, whereas in most cases the amount was 0.1 mg. or less. These results show that the true silicon content of this iron is of the order of 0.002 per cent, as compared with 0.0005 per cent or less indicated by dehydration with sulfuric acid.

ACKNOWLEDGMENT

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Determination of Boron Spectroscopically

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THE essential nature of boron in plant metabolism has been ascertained physiologically by several investigators. Bertrand and Agulhon (2, 3, 4) have demonstrated the presence of the element in normal tissues of various species of plants and animals. Jay (7), investigating the occurrence of boron in natural foods, found it to be widely distributed. Tests for boron in plant and animal tissues have, for the most part, been measurements of the depth of color imparted to standardized strips of turmeric paper. Details of methods using turmeric, curcumin, and tincture of mimosa blossoms have been described by several investigators (4, 5, 6, 8). These methods are very sensitive to small quantities of boron, but are only roughly quantitative. Bertrand and Agulhon (2) confirmed their results with turmeric paper by spectroscopic examination of the color imparted to the flame of burning hydrogen.

The green color imparted to the flame of burning alcohol is a very sensitive test for boron. To test for boron in the presence of other compounds producing a green flame, Bordas and Touplain (6) vaporized the acid solution of the sample in methyl alcohol and ignited the vapor at the end of a glass tube. Boric acid with methyl alcohol in the presence of a dehydrating acid forms methyl borate, $(CH_3)_2BO_3$. The difference in the boiling points of the boric acid ester and of methyl alcohol is $1^\circ C.$, and it has been found that with small amounts of the ester present the boiling point is constant.

Spectroscopic examination of the flame of the mixed vapors of the alcohol and ester showed four bands between the sodium line and the first blue caesium line, the most intense being close to that of thallium in the green portion of the spectrum. With less than 0.033 gram of boron per liter of alcohol, it was found that the bands were not

A new spectroscopic method for the determination of boron is described. The procedure consists in ashing the plant material at a low temperature in the presence of an excess of an alkali, and dissolving the ash in a solution of citric acid. Boron is separated from the solution of salts by converting it into methyl borate and distilling. The methyl borate is burned in oxygen by a special type of apparatus and the spectrum absorbed by the addition of a standard solution of potassium permanganate from a buret into a glass cell containing distilled water and converting the permanganate factor to its equivalent in boron. Extreme sensitivity was obtained by burning the methyl borate in an atmosphere of oxygen. Boron can be determined quantitatively on samples of plant tissues containing 0.05 to 0.3 mg. of boron with an accuracy of ± 0.0095 mg.

visible. Increase in the boron content of the solution resulted in a spectrum of greater intensity. To measure the relative intensity of the spectrum, a number of solutions of colored salts were tried as light filters. A dilute solution of potassium permanganate as well as solutions of several organic dyes were capable of absorbing the green portion of the spectrum. Potassium permanganate was considered the most suitable because it can be standardized readily, and is the least subject to change under laboratory conditions.

Measurement of the intensity of the spectrum was effected by adding 0.01 *N* potassium permanganate solution from a buret to 50 ml. of distilled water in a glass cell placed between the spectroscope and the flame, until the band was just eliminated. Ten milliliters of acid alcohol containing a known amount of boron were placed in a 50-ml. Erlenmeyer flask fitted to a short hard glass tube fixed in a glass chimney (Figure 1). Two glass tubes projecting from the chimney fixed the distance of the spectroscope from the flame at 6 cm. and supported a cell of 2 cm. thickness under a buret. The flask was immersed in a constant-temperature water bath, and the temperature was raised until the flame was 1.5 cm. high. A direct-vision Schmidt and Haensch spectroscope was placed before the cell, and 0.01 *N* potassium permanganate solution was added slowly, with stirring, until the first green band of the spectrum was absorbed. It was found that a definite normality of potassium permanganate solution 2 cm. thick would just eliminate the lines from the spectrum produced by the presence of a definite quantity of boron in the solution, other conditions being identical.

Conditions other than the quantity of boron present that might affect the intensity of the spectrum were investigated.

It was found (Table I) that the distance of the spectro-

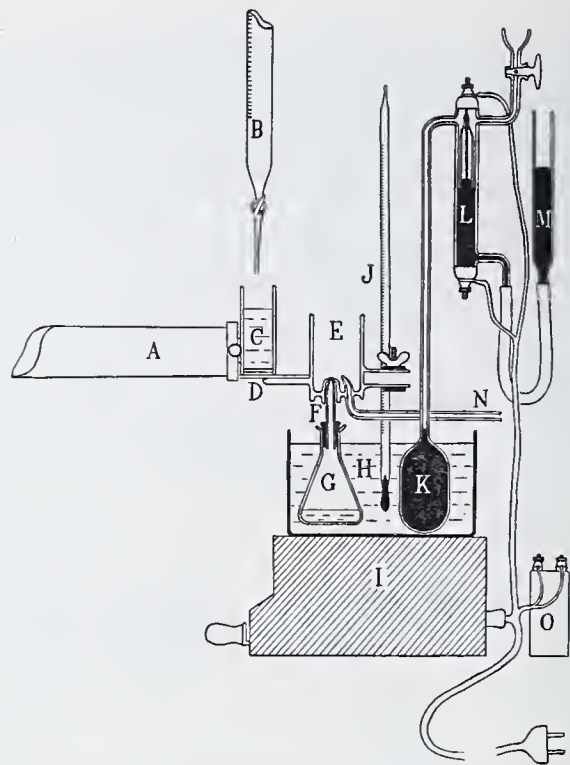


FIGURE 1. APPARATUS FOR SPECTROSCOPIC DETERMINATION OF BORON

- A. Spectroscope

B. Buret

C. Cell

D. Support

E. Chimney

F. Burner

G. Sample flask

H. Bath

I. Heater

J. Thermometer

K. Mercury bulb

L. Thermostat

M. Regulation

N. Pilot light

O. Condenser

scope from the flame affected the intensity of the spectrum, especially with the smaller quantities. This distance was fixed at 6 cm. by glass stops for all determinations. The position of the cell did not exert any noticeable influence so long as it was perpendicular to the spectroscope. Differences in the height of the flame resulted in different intensities, the intensity decreasing as the size of the flame increased. The flame must be over 1 cm. in height in order to burn smoothly and quietly. This was accomplished by heating the bath slowly until the top of the flame was just opposite the 1.5-cm. mark on the chimney, and adjusting the thermostat for this temperature. The setting of the slit of the spectroscope also influenced the intensity by varying the amount of light admitted. It was opened until the bands were sharp, and set at the same figure for all determinations. Dissolved salts, platinum wire, and other catalysts exert a minor influence that is overcome by the presence of 5 per cent phosphoric acid in the alcohol. The effect is due to hastening the formation of methyl borate.

The difference in the boiling points of the alcohol and ester did not affect the intensity for quantities of boron within the range of the method. The amounts of potassium permanganate solution required for a given amount of boron were checked 15 minutes after igniting the vapor. The curve (Figure 2) shows the exact quantities of 0.01 *N* potassium permanganate solution necessary to produce sufficient color in 50 ml. of water to absorb the first green band of the spectrum of known amounts of boron. The position of each point measured on the curve is the average of from three to five determinations.

A table showing the boron equivalent of each 0.1 ml. of 0.01 *N* potassium permanganate solution can be prepared by calculations from the data on known quantities of boron for convenience in converting buret readings to grams per liter of boron.

TABLE I. MINOR FACTORS INFLUENCING INTENSITY OF SPECTRUM

FACTOR	POTASSIUM PERMANGANATE SOLUTION, 0.01 <i>N</i>		
	B = 0.05	B = 0.10	B = 0.5
	gram/liter	gram/liter	gram/liter
1. Distance of spectroscope from flame			
3 cm.	4.8	7.1	10.15
6 cm. ^a	4.6	7.0	10.1
8 cm.	4.2	6.8	9.9
2. Position of cell			
Against chimney	4.6	7.1	10.1
Against spectroscope ^a	4.6	7.0	10.1
Intermediate	4.6	7.0	10.05
3. Height of flame			
0.5 cm.	5.0	7.3	10.7
1.0 cm.	4.7	7.0	10.4
1.5 cm. ^a	4.65	7.0	10.1
3.0 cm.	4.5	6.9	9.95
4. Opening of slit			
Slight (Na to 3060)	4.1	6.7	10.0
Moderate (Na to 3053) ^a	4.6	7.0	10.15
Wide (Na to 3045)	4.8	7.2	10.3

^a Found to be most satisfactory condition.

The practice of adding boric acid or borates to foods as preservatives has been responsible for the development of several methods for the extraction of boron from plant material. These methods are commonly used in conjunction with volumetric or gravimetric determinations, and were found to be unsatisfactory for the analysis of minute quantities, as small losses occur in the preparation of the sample. It was found that losses may occur on ignition above 800° C. and on evaporation of the acid solution.

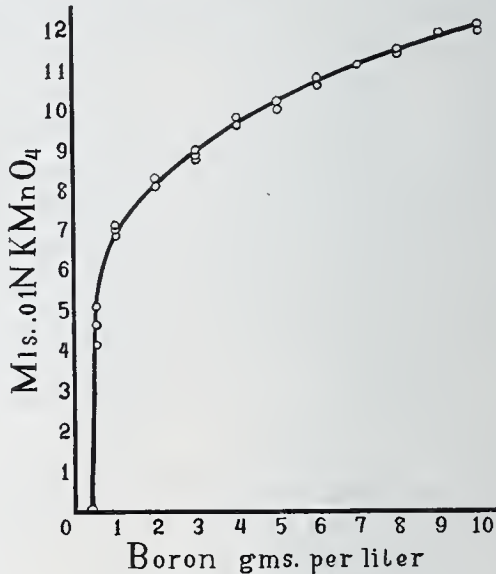


FIGURE 2. POTASSIUM PERMANGANATE SOLUTION REQUIRED TO ELIMINATE FIRST GREEN BAND FROM SPECTRA OF BORON BURNED IN AIR

Table II shows recoveries from salt mixtures comparable to plant ash.

TABLE II. EXTRACTION OF BORON IN PRESENCE OF Ca, Mg, AND K IN HCl SOLUTION

TREATMENT	B PRESENT	B RECOVERED
	Gram	Gram
Evaporated (acid), extracted with methyl alcohol, and filtered	0.0016 0.0035	0.0002 0.0005
Evaporated with K ₂ CO ₃ , extracted with methyl alcohol, and filtered	0.0016 0.0035	0.0008 0.0020
Evaporated with methyl alcohol containing 25% NH ₄ OH, extracted with methyl alcohol, and filtered	0.0016 0.0035	0.00097 0.00294
Evaporated with methyl alcohol containing 25% NH ₄ OH, extracted with methyl alcohol for 3 hours in Soxhlet tube	0.0016 0.0035	0.00167 0.00343

Evaporation of acid solutions on the water bath results in a loss of boron amounting to 75 per cent or more, if very small quantities are present. The addition of an alkali

to the solution prevents losses on evaporation, but forms precipitates insoluble in water and methyl alcohol that interfere with the quantitative extraction of boron by the alcohol. The precipitation of insoluble compounds by an alkali in the presence of considerable methyl alcohol does not present this difficulty if the alcohol is added slowly to the cold solution. By evaporating with small additions of alcoholic ammonia, approximately 90 per cent of the boron present will be easily soluble in methyl alcohol, and practically 100 per cent can be recovered by extracting for 3 hours in a Soxhlet tube.

Determinations of plant material gave similar results to those obtained with salt mixtures. The recoveries from additions of boron (boric acid) to watercress are given in Table III.

TABLE III. RECOVERY OF ADDED BORON FROM WATERCRESS

(Average of three 25-gram samples)			
TREATMENT	B ADDED Gram	B PRESENT Gram	B FOUND Gram
Ashed 750° F.	0.003
Ashed 750° F.	0.001	0.004	0.00393
Ashed 750° F.	0.002	0.005	0.00517
Ashed 750° F.	0.005	0.008	0.00798
Ashed 850° F.	...	0.003	0.003
Ashed 850° F.	0.001	0.004	0.00375
HCl soln. of residue of previous extraction	None
HCl soln. of fused silicates	None

To avoid the handling of large quantities of salts insoluble in methyl alcohol and the extraction of soluble salts other

than borates, distillation was substituted for extraction by using the apparatus shown in Figure 3. The sample (plant ash) was dissolved in an excess of citric acid and transferred to flask *C*, using approximately 20 ml. of water. Washing was completed with methyl alcohol (30 to 40 ml.) and the flask connected. Flask *F* contains 0.1 ml. of 0.5 *N* potassium hydroxide in 10 ml. of distilled water. Boron is absorbed by the solution in *F* from the vapors produced in *C*. The alcohol vapor is condensed in the reflux *A* and returned to flask *C*. The boiling point is higher in flask *C* and the alcohol is completely condensed, resulting in a major portion of the alcohol being retained in flask *C*. Boron was completely extracted from plant ash by this method in 1.5 hours. Boron could not be found in the small washing tube at the top of the condenser even when relatively large quantities of boron were distilled.

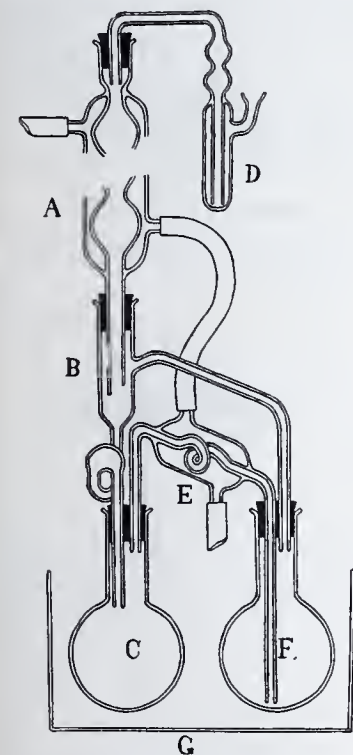


FIGURE 3. APPARATUS FOR SEPARATION OF BORON BY DISTILLATION

- A. Condenser
- B. Adapter
- C. Sample flask
- D. Absorption tube
- E. Condenser
- F. Receiver
- G. Water bath

The procedure for plant material found to be the most rapid and accurate is as follows:

Weigh a sufficient quantity of the ground sample of plant material (calculated to the moisture-free condition) to give 0.0005 to 0.005 gram of boron. If the plant material yields an acid ash, add sufficient potassium carbonate to make the ash alkaline, and char in a silica dish over a low flame. Ash

the sample in a muffle furnace at or below 400° C. Cool in a desiccator, moisten the ash with distilled water, cover with a watch glass, and add a strong solution of citric acid with a finger pipet until the solution is strongly acid. Wash into the extraction flask with a small quantity of water and 30 to 35 ml. of methyl alcohol. Add 0.1 ml. of 0.5 *N* potassium hydroxide to 10 ml. of distilled water in the second flask, and distil for 1.5 hours. Wash the alkaline solution into

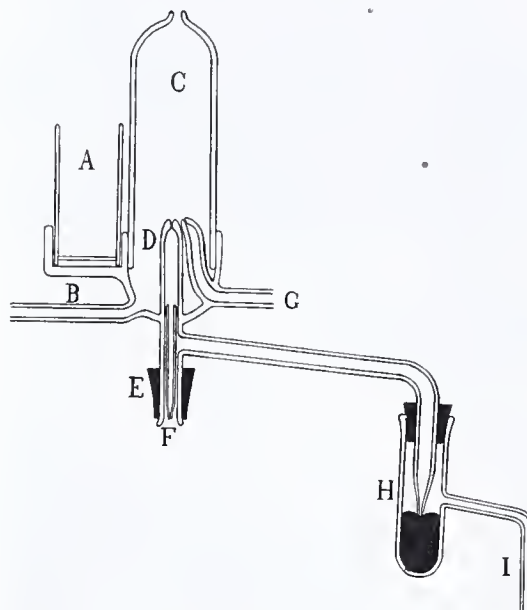


FIGURE 4. APPARATUS FOR BURNING METHYL BORATE IN OXYGEN

- A. Cell
- B. Oxygen inlet
- C. Chimney
- D. Microburner
- E. Connection for flask
- F. Vapor inlet (capillary)
- G. Gas inlet for pilot light
- H. Pressure regulator
- I. Alcohol overflow

a 50-ml. dish, add 5 ml. of ammonium hydroxide, and evaporate to dryness on the water bath. Dissolve the residue in 5 per cent phosphoric acid in methyl alcohol, and make up to a suitable volume with acid alcohol at 20° C. Transfer to an Erlenmeyer flask, connect to the burner, and, after the flame meets the prescribed conditions of 1.5 cm., add 0.01 *N* potassium permanganate solution to 50 ml. of water in the cell until the bright green band of the boron spectrum is eliminated. Refer the required quantity of potassium permanganate solution to a table showing grams of boron per liter for the quantity present, and divide by the weight of the sample to obtain the per cent of boron present (grams of boron per liter $\times 10/1000 \times 100/\text{sample}$). The table showing grams per liter of boron present for any quantity of potassium permanganate solution used should be prepared by the operator from known quantities of boron, because the sensitivity of different spectrometers and their adjustments vary widely. Reagents used must be free from boron.

The method is also applicable to the determination of boron in animal tissue and waters as well as plant tissues by slight modifications of the procedures for obtaining the boron in suitable form for solution in methyl alcohol.

The method is sensitive to much smaller quantities of boron if the vapors are burned in an atmosphere of oxygen. Figure 4 shows the apparatus used for burning methyl alcohol-methyl borate vapors in oxygen under controlled conditions. The quantity of vapor burned in oxygen is greater than in air and cannot be controlled by the size of the flame, as marked changes in the rate of vaporization make but slight differences in the size of the small, hot flame. To insure the burning of the vapor at the same rate in each determination, constant pressure was kept in the distillation flask by a mercury valve and capillary tube. The tubes *D* and *G* are of thick-

walled hard glass tubing (not Pyrex). Attempts at sealing these tubes (and *B*) into a glass support for the cell and chimney were unsatisfactory, so a rubber stopper and a short glass collar of slightly greater diameter than the chimney

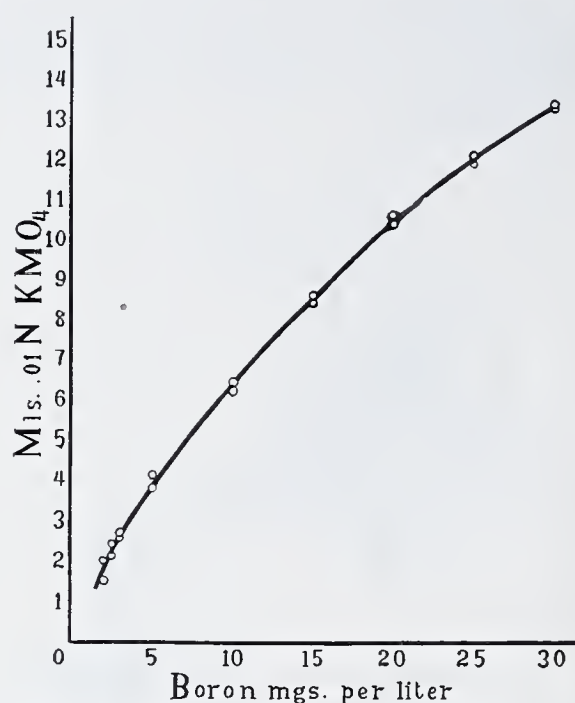


FIGURE 5. POTASSIUM PERMANGANATE SOLUTION REQUIRED TO ELIMINATE FIRST GREEN BAND FROM SPECTRA OF BORON BURNED IN OXYGEN

were substituted. A metallic base supported with a ring-stand clamp is recommended for the introduction of the gas tubes and support of the cell and chimney. The chimney is of heat-resistant glass. An unsteady flame due to currents of oxygen can be avoided by placing glass wool in the bottom of the chamber.

Figure 5 shows the grams per liter of boron in methyl

alcohol represented by any quantity of 0.01 *N* potassium permanganate solution within the limits of the method.

The possibility of replacing the buret and cell with a scale and sliding glass wedge similar in color to potassium permanganate solution was considered but was not investigated. The use of the wedge would probably simplify the absorption of the spectrum and shorten the method, but to approach the accuracy of the buret and cell, the lengths of the scale and wedge would probably be too great for convenience. The spectroscopic method by burning in oxygen will detect the presence of less than 0.5 part per million of boron in methyl alcohol. Quantities of boron between 3 and 30+ parts per million can be determined quantitatively with an accuracy of ± 0.35 part per million.

Plant materials could not be checked as accurately as could solutions of boric acid, but could be checked within the limits of ± 0.95 part per million, or ± 0.000095 per cent on a moisture-free basis.

The method of Wilcox (10) and the A. O. A. C. (1) volumetric method were not applicable to the determination of such minute quantities of boron as occur in normal plant tissues. The low buret readings on extremely large samples of plant material and the necessity of two additions of standard alkali resulted in a wide range of inaccuracy.

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An Esterification Resin as a Ground-Joint Lubricant

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IN A paper by Bruun and Schicktanz (1), mention is made of the use of a mixture of diethylene phthalate and triethylene phthalate resins as a stopcock lubricant for use in contact with petroleum distillates. Although this mixture was found to have the desired consistency and stability for a ground-joint lubricant, it was not adapted for use with distillates rich in the aromatic hydrocarbons, since these resins are readily soluble in benzene and toluene. It was found that a resin made with a polyglycol and a tri-reactive acid, in which the esterification was allowed to proceed only to the fusible stage, provided a lubricant having the proper viscosity which was insoluble in both the aromatic and aliphatic hydrocarbons.

One mole of citric acid and 1.5 moles of tetraethylene glycol were heated together at 180° to 185° C. for 90 minutes. The flask was then removed from the oil bath and allowed to cool to room temperature. Prolonged heating of this mixture results in an infusible product. The resin obtained was clear, amber-colored, of balsam consistency, and possessed marked adhesiveness. It was found to be readily soluble in water, alcohol, and acetone, but insoluble in petroleum ether and toluene. Chemical analysis indicated about 65 per cent esterification.

When applied by the customary technic to ground joints, it provided a satisfactory seal in contact with petroleum distillates over considerable periods of time with no tendency to become thin, and of low lubricating value. In contrast with many lubricants suggested for this purpose, the resin offers greater stability, is chemically inert, and may be kept indefinitely without changes occurring in its properties.

Tetraethylene glycol, $\text{CH}_2\text{OH}(\text{CH}_2\text{OCH}_2)_3\text{CH}_2\text{OH}$, may be synthesized from ethylene oxide and triethylene glycol in a pressure reaction. It boils at 190° C. at 3-mm. pressure. The presence of the long chain separating the two reactive groups imparts fluidity when it is used as a resin base. A similar resin made with citric acid and triethylene glycol was more viscous and, when used at room temperature, presented too much resistance to turning of the stopcock.

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Determination of Beeswax in Candles

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IN ASCERTAINING the constants of beeswax and of candle mixtures, the determination of the saponification number seems to be the one about which the authors disagree most as regards detailed procedures, and the analyst who reads the considerable volume of literature on this general subject (1, 3, 6, 7, 8, 10, 12, 14) is inclined to agree with Werder (16) when he complains about the many different methods that have been suggested for this particular determination. Winkler (17), however, is about the only one who presents detailed experimental proof for his particular procedures. Having been called upon some years ago to conduct a good many "candle analyses," we were struck with this abundance of methods and paucity of experimental evidence, and after considerable preliminary experimentation we fixed upon a certain detailed procedure which we are satisfied gives accurate results.

DETERMINATION OF SAPONIFICATION NUMBER

In Table I is summarized the method recommended as giving quantitative saponification in the shortest time, using potassium hydroxide in absolute ethyl alcohol, which the authors consider the easiest, cheapest, and most accurate alkali to work with.

TABLE I. SUMMARY OF METHOD

SUBSTANCE	STRENGTH OF ALKALI <i>N</i>	VOL. OF ALKALI <i>Cc.</i>	WT. OF SAMPLE	TIME OF BOILING <i>Hours</i>	1% PHENOL-PHTHALEIN USED AS INDICATOR
					<i>Cc.</i>
Candle mixtures	0.5	40-50	3.5 ± 0.4 gr.	2.5	1
Pure beeswax	1	40-50	3.5 ± 0.4 gr.	2	1

The saponification together with the subsequent titration is carried out in 500-cc. Pyrex Kjeldahl flasks. Refluxing is provided for by fitting them with test-tube condensers connected in series to the water supply (5). The flasks are boiled on an asbestos gauze over a Bunsen flame at such a speed that the solvent drops back into the boiling mixture at the rate of about 2 drops per second. The sides of the flasks are protected against overheating by placing over the gauze a square of asbestos in which a hole about 4.5 cm. in diameter has been cut, thus allowing only the bottom of the flask to get the direct heat of the gauze. After boiling, the indicator is added and the mixture titrated boiling hot with carefully standardized hydrochloric acid of the same strength as the alkali used.

The following precautions must be observed: The burets must be accurately calibrated, and the one containing the alcoholic solution should be allowed to drain 10 minutes before reading. The alkali after filtering must be kept in a tightly stoppered brown bottle and its potassium hydroxide equivalent checked frequently by running at least two blanks in exactly the same way as the saponification itself is conducted. The wax sample should be introduced in the form of a little ball, weighed to the nearest milligram, and a few small glass beads added to insure quiet boiling. The determination must be run in duplicate and, in case these do not agree within about a milligram, another pair should be run.

Once a certain sample weight and a certain kind and quan-

tity of alkali solution have been decided upon, completeness of saponification can be proved only by running a time series. These series were run with one *N* and with 0.5 *N* solutions of potassium hydroxide in absolute ethyl alcohol on the same sample of beeswax, and then on two common candle mixtures of known composition and constants. The results are summarized in Table II.

TABLE II. RESULTS OF TIME SERIES

SAPONIFYING SOLN.	TIME OF BOILING <i>Hours</i>	NO. OF INDIVIDUAL DETNS. MADE	AV. SAPONIFICATION NO.
PURE BEESWAX			
1 <i>N</i> KOH	0.5	4	96.2
1 <i>N</i> KOH	1	4	96.4
1 <i>N</i> KOH	2	4	98.2
1 <i>N</i> KOH	3	4	98.3
0.5 <i>N</i> KOH	1	2	93.9
0.5 <i>N</i> KOH	2	6	97.9
0.5 <i>N</i> KOH	3	6	98.0
COMMON CANDLE MIXTURE ^a			
1 <i>N</i> KOH	0.5	4	111.0
1 <i>N</i> KOH	1	4	112.5
SECOND KNOWN CANDLE MIXTURE ^b			
1 <i>N</i> KOH	0.5	2	44.0
1 <i>N</i> KOH	1	2	44.0
1 <i>N</i> KOH	2	5	45.4
1 <i>N</i> KOH	3	3	46.0
0.5 <i>N</i> KOH	3	3	46.3

^a Beeswax, 51 per cent; stearic acid, 30 per cent; paraffin, 19 per cent; calcd. saponification no., 112.2.

^b Beeswax, 15 per cent; stearic acid, 15 per cent; paraffin, 70 per cent; calcd. saponification no., 45.8.

Complete time series were not run on other saponification media, but one *N* potassium hydroxide in absolute methanol and one *N* sodium ethylate gave satisfactory results in 2 hours, as might be expected, and the results of Kettle (11), who uses one *N* potassium hydroxide in isopropyl alcohol to saponify beeswax in 10 minutes were also confirmed. However, unless time is the primary consideration, this method is not recommended, as the isopropyl alcohol, besides being more expensive to buy, cannot be recovered profitably from the saponification mixtures as can ethyl alcohol, about 75 per cent of which can be recovered by the use of a 2-foot Vigreux column.

DETERMINATION OF ACID NUMBER

The conditions for accuracy for this determination are the use of a fairly large sample, on account of the small numerical value of this constant for most candle mixtures, and the use of an alkali which does not induce appreciable saponification. As these conditions are easily met, most of the methods given in the literature will be found suitable. A good method is titrating a 10-gram sample dissolved in 250 cc. of 95 per cent ethyl alcohol with 0.5 *N* aqueous potassium hydroxide solution, using 10 drops of one per cent phenolphthalein as indicator, and finishing at a noticeable pink color which persists on half a minute's boiling. A blank is run on the alcohol. This treatment causes no appreciable hydrolysis of the esters present unless the mixture contains about 35 per cent or more Japan wax. Pure Japan wax is so easily hydrolyzed that its acid number had to be determined by dissolving 2.5 grams of it in 250 cc. of carbon tetrachloride and titrating the warm solution with 0.1 *N* sodium ethylate; the end point lasted about a minute.

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INTERPRETATION OF RESULTS

The practice of using beeswax candles in the liturgy of the Catholic Church can be traced far back into Christian antiquity, but the actual decree of the Sacred Congregation of Rites which gives rise to this particular analytical problem dates from 1904 (2). The passage of interest to the chemist may be translated as follows: ".....the Paschal candle, the candle used in blessing the baptismal water, and the two candles lit on the altar during Mass are to be of beeswax, at least in largest part (maxima pars); the other candles on the altar should be either in greater part or of a noticeable proportion of the same wax." This "maxima pars" is usually taken to mean 51 per cent. The following compositions are common in American candles sold for church use:

	%	%	%	%	%
Beeswax	100	60	51	13	15
Stearic acid	...	20	30	37	15
Paraffin	...	20	19	50	70

In examining candles made by any reputable American manufacturer, it may be assumed that they contain only these three substances; and as the only esters in a ternary mixture of this kind are present in the beeswax, analysts usually calculate the percentage of this substance by using the principle given by Hehner (9), although not in exactly the same form as he published it. Since the stearic acid, if any, affects both the acid number and the saponification number equally, the percentage of beeswax may be calculated from the expression:

$$\% \text{ beeswax} = \frac{\text{ester number of candle}}{\text{ester number of beeswax}}$$

For example, in the case of the 51 per cent candle used in one of the time series (Table II) and whose acid number was found to be 75.1, we have

$$\% \text{ beeswax} = \frac{112.5 - 75.1}{73.1} = 51.2\%$$

From this the amount of stearic acid is calculated to be 30.0 per cent, and that of the paraffin (by difference) to be 18.8 per cent. Comparison with the actual composition of this mixture (which was unknown to the analyst) shows very satisfactory agreement, and about of the order to be expected when the procedure is conducted carefully and the constants of the candle ingredients are known. As a rule, however, these are not known, hence no analysis of this kind should be "guaranteed" closer than 5 per cent. As regards the value for the ester number of beeswax, a minimum value evidently works to the favor of the manufacturer, yet to be fair to the purchaser as well, it is customary to use the value of 72 for this constant (when it is not known), this being its lowest value given by the U. S. P.

In case the candle seems to be composed of other substances than the three mentioned, the chemist will find the problem (which may become very complicated) treated quite adequately in the literature cited, to which may be added the general method given by Elser (4) based on the melting points of the products obtained by the fractional crystallization of the candle mixture from benzene, and also the method of Watson (15) for estimating carnauba wax. A glycerol test (qualitative at least) should always be run on a large sample of all candle mixtures to see if any Japan wax is present, from which "synthetic beeswax" may be made (13) which can simulate exactly the ester number of true beeswax. It has been our experience, however, that candles notably below par in beeswax content are made so by the addition to the beeswax of unduly large amounts of stearic acid and paraffin, rather than by the substitution of any other ingredients for the beeswax itself. In fact, so far we have not met with any indications of dishonest prac-

tice in cases where the beeswax content was stamped on the candle.

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Atomic Weights 1932

In response to requests of readers, we reprint here from the *Journal of the American Chemical Society* for April, 1932, page 1277, the second report of the Committee on Atomic Weights of the International Union of Chemistry, of which G. P. Baxter is chairman.

ATOMIC				ATOMIC			
SYM-	NUM-	ATOMIC		SYM-	NUM-	ATOMIC	
BOL	BER	WEIGHT		BOL	BER	WEIGHT	
Aluminum	Al	13	26.97	Molybdenum	Mo	42	96.0
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.93	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.8
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	31.02
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.10
Carbon	C	6	12.00	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Radium	Ra	88	225.97
Cesium	Cs	55	132.81	Radon	Rn	86	222
Chlorine	Cl	17	35.457	Rhenium	Re	75	186.31
Chromium	Cr	24	52.01	Rhodium	Rh	45	102.91
Cobalt	Co	27	58.94	Rubidium	Rb	37	85.44
Columbium	Cb	41	93.3	Ruthenium	Ru	44	101.7
Copper	Cu	29	63.57	Samarium	Sm	62	150.43
Dysprosium	Dy	66	162.46	Scandium	Sc	21	45.10
Erbium	Er	68	167.64	Selenium	Se	34	79.2
Europium	Eu	63	152.0	Silicon	Si	14	28.06
Fluorine	F	9	19.00	Silver	Ag	47	107.880
Gadolinium	Gd	64	157.3	Sodium	Na	11	22.997
Gallium	Ga	31	69.72	Strontium	Sr	38	87.63
Germanium	Ge	32	72.60	Sulfur	S	16	32.06
Gold	Au	79	197.2	Tantalum	Ta	73	181.4
Hafnium	Hf	72	178.6	Tellurium	Te	52	127.5
Helium	He	2	4.002	Terbium	Tb	65	159.2
Holmium	Ho	67	163.5	Thallium	Tl	81	204.39
Hydrogen	H	1	1.0078	Thorium	Th	90	232.12
Indium	In	49	114.8	Thulium	Tm	69	169.4
Iodine	I	53	126.932	Tin	Sn	50	118.70
Iridium	Ir	77	193.1	Titanium	Ti	22	47.90
Iron	Fe	26	55.84	Tungsten	W	74	184.0
Krypton	Kr	36	83.7	Uranium	U	92	238.14
Lanthanum	La	57	138.90	Vanadium	V	23	50.95
Lead	Pb	82	207.22	Xenon	Xe	54	131.3
Lithium	Li	3	6.940	Ytterbium	Yb	70	173.5
Lutecium	Lu	71	175.0	Yttrium	Y	39	88.92
Magnesium	Mg	12	24.32	Zinc	Zn	30	65.38
Manganese	Mn	25	54.93	Zirconium	Zr	40	91.22
Mercury	Hg	80	200.61				

A New Vacuum-Furnace Design

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EXPERIMENTATION under conditions of high temperature and high vacuum involves numerous difficulties. Many of the older types of furnaces are a source of continual trouble because of mechanical imperfections and unsuitable operating characteristics, and necessitate a constant battle by the experimenter against vacuum leaks and electrical derangements. Consequently the efficiency of such experimentation suffers.

The Pacific Experiment Station, in connection with its program of specific heat measurements at high temperatures on metals and metallurgically important compounds, recently completed the construction and testing of a new vacuum furnace for calorimetric measurements at high temperatures. The design adopted has several new features which greatly improve the ease and certainty of experimentation.

DESCRIPTION OF FURNACE

The furnace is an electrically heated, water-cooled type, 76 cm. long and 40.5 cm. in diameter. It has been built of unit parts in such a manner that it may be repaired or altered easily and economically. Figure 1 shows a cross section, a plan of the jacket-head, and the design of the construction for bringing out electrical lead wires.

VACUUM JACKET. The vacuum jacket consists of two concentric cylindrical shells of heavy steel pipe, the outer shell, *A*, being 0.64 cm. thick, and the inner shell, *B*, 1.59 cm. thick, surmounted by a heavy, removable head. The cylindrical shells have welded boiler-plate bottoms and are held together at the top by a circularly split ring, *C*, which is screwed on the outside of the inner shell and on the inside of the outer shell. The two parts of this ring telescope with a driving fit, which enables the jacket to be taken apart by applying a few pounds of air pressure between the walls and to be assembled by applying a vacuum similarly. The pressure or vacuum required is less than one atmosphere. This arrangement has been found to be of great value in that it permits easy repair of minute leaks which may develop.

The jacket-head consists of a bottom of 1.59-cm. boiler plate and a top of 0.95-cm. boiler plate separated by a ring cut from a section of 30.5-cm. pipe 0.95 cm. thick, the width being 3.18 cm. The head is assembled with 0.64-cm. ($\frac{1}{4}$ -inch) S. A. E. cap screws, *E*, which pass through the top plate and screw into the bottom plate. A cork gasket and cement are used on each side of the ring. The head is fastened to the jacket by 1.11-cm. ($\frac{7}{16}$ -inch) S. A. E. cap screws, *D*, and is recessed at *F* to fit the projecting upper end of the inner jacket shell. A fiber gasket was found to be satisfactory

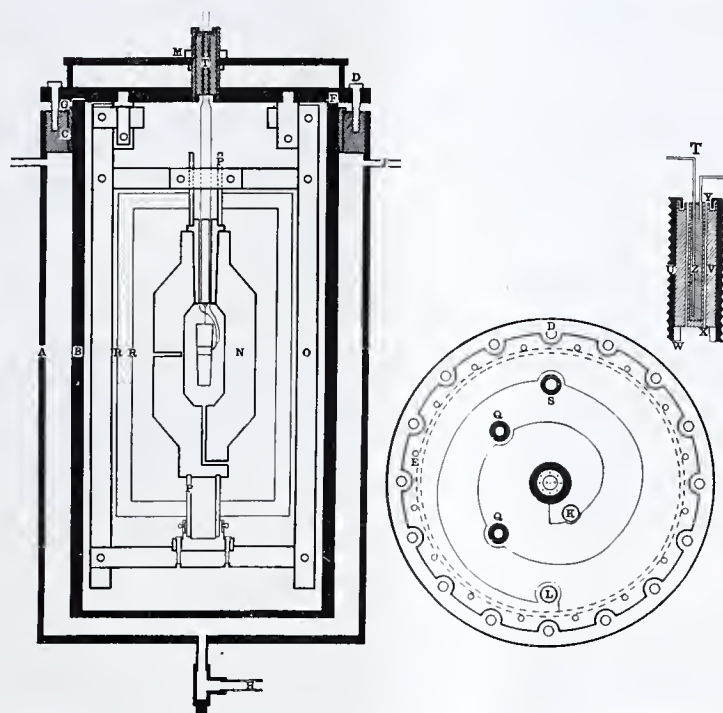


FIGURE 1. DIAGRAM OF FURNACE AND IMPORTANT PARTS

in this recess. A narrow bearing surface 0.95 cm. wide enables satisfactory compression of the gasket to be secured. A simple arrangement of rubber and metal bands (not shown in the diagram) is incorporated for filling annular space *G* with mercury to assure the gas-tightness of this joint for work at very high vacuums.

The cooling water enters the jacket through tube *H*, passes out tubes *J*, enters the head through tube *K*, and leaves by tube *L*. A metal spiral (shown in the plan of the head) assures the absence of dead spaces, a precaution that experience has proved to be essential for satisfactory cooling of the gaskets and lead-out wire seals.

HEATER. At present the furnace contains a copper block, *N*, of some 22 kg. mass, which is heated by a coil of nichrome ribbon of 8 ohms resistance, wound helically, and insulated by alundum cement of the grade used for platinum-wound furnaces. This block is supported by framework *O* of 2.54-cm. (1-inch) square cold-rolled steel suspended from the head, and is held in place and thermally insulated by porcelain tubes *P*. For other purposes any suitable heating coil may be similarly installed.

The heater lead wires pass through the compression-joint tubes *Q*, which are of a special type and will be described later.

The heater unit is surrounded by two thin 0.04-cm. (27-gage) monel metal radiation shields, *R*, which also are supported by frame *O*.

JOINTS AND SEALS FOR LEAD WIRES AND VACUUM CONNECTION. The heater lead tubes *Q*, evacuation tube *S*, and fitting *T*, through which thermocouples and other lead wires pass, are threaded and screwed into holes in the bottom plate of the head and are soldered to it on the upper side. This is necessary since all the joints must be vacuum-tight at this point. At the junctions with the upper plate of the head, which need be water-tight only, two nuts screwed to each tube and a gasket below the plate, such as shown at *M*, were found to make satisfactory, removable, and water-tight seals.

The tubes for the heater leads are beveled in at the top to form wells and hold close-fitting Pyrex glass tubes, which extend just below the head. The heater wires are enclosed by the glass and the wells filled with de Khotinsky cement.

Fitting *T* for the thermocouple leads consists of an outer heavy copper tube, *U*, and a close-fitting copper cylinder, *V*, held in place by split-ring nut *W*. The thermocouples are brought out through Pyrex glass tubes held in holes *X*, and well *Y* is filled with de Khotinsky cement. *Z* is a hollow copper cylinder set in *V* and equipped with tubes

for water cooling, which gives additional protection to the de Khotinsky seal.

OPERATION OF FURNACE

The furnace operates for all except the highest vacuums without using the mercury seal. No difficulty was encountered in pumping out to a pressure of 0.002 mm. of mercury at room temperature with a good oil pump. In the neighborhood of 1000° C., which is about as high a temperature as may be reached safely with the copper block, the apparatus pumped down to 0.1 mm. of mercury after small amounts of impurities in the copper had been removed by distillation and the original rapid degassing of metal and alundum cement had diminished.

The heating unit and monel metal shields proved to be entirely satisfactory, 4.5 and 13.8 amperes through the 8-ohm coil giving, respectively, temperatures of 412° and 906° C.

The experience with this furnace has definitely proved the great value of radiation shields. Monel metal was used because it retains a good reflecting surface after being heated *in vacuo* to temperatures around 1000° C., and has a relatively low thermal conductivity. On dismantling the apparatus, the outer shield had the appearance of never having

been hot, which is substantiated by the fact that the temperature of the cooling water was only slightly higher on leaving the furnace than on entering. In reducing the heat losses, the radiation shields also protect the de Khotinsky seals, which were a great source of trouble in a previously used furnace which was not equipped with radiation shields completely surrounding the heater unit.

The method of bringing out lead wires also proved very satisfactory and is considered a marked improvement over methods formerly employed. Fitting *T* was constructed to give good thermal contact between copper cylinder *V* and copper tube *U*, which is surrounded by the cooling water. This construction, with the cooling unit *Z*, makes practically certain the permanence of the de Khotinsky seal in well *Y*.

ACKNOWLEDGMENT

The success of this furnace is largely due to designs contributed by C. C. Maier, supervising engineer of the Pacific Experiment Station, and to the excellent workmanship of C. M. Bell, mechanic at the Pacific Experiment Station.

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Determination of Fluorine and Boron in Organic Compounds

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IN SOME of the researches being carried on in this department on organic boron trifluoride compounds, the problem of finding a dependable method of analysis for both fluorine and boron arose. A number of more or less unsuccessful attempts to do this have been made in the past. Kraus and Brown (4) prepared various amino derivatives of boron trifluoride, and analyzed them for fluorine, boron, and nitrogen, in establishing their structures. Their analyses for fluorine and boron indicate the need of a more reliable method. Bowlus and Nieuwland (1) were able to analyze for boron with an average error of about 6 per cent, by decomposition of the sample through continued heating with fuming nitric acid in a sealed tube, and titrating the boric acid formed with base and mannitol, according to the standard procedure (5). These authors did not report fluorine on the analyses. Vaughn and Nieuwland (10) presented a new method of analysis for organic fluorides, using sodium in liquid ammonia, but boron was not present in their compounds.

There are a number of difficulties peculiar to the analysis of compounds containing boron and fluorine. Fusions of the samples with alkali carbonates (6) proved to be unsuccessful, as there was difficulty in decomposing the compounds, and there was evidently some loss through volatilization. It was finally decided to destroy the organic matter by combustion in a Parr sulfur bomb with an oxidizing mixture of sodium peroxide, potassium chlorate, and sugar. Most of the organic boron trifluoride compounds are deliquescent fuming substances, liquids or solids, which interact instantly with the fusion mixture. Recourse was had to weighing them in gelatin capsules and placing them in the bomb, thus inclosed. The capsules were completely destroyed by the ignition and did not interfere with quantitative combustion of the compound.

When the products of the fusion were dissolved in water, a solution containing a high concentration of alkali hydroxide and carbonate was obtained, and these interfered with the precipitation of calcium fluoride. When an attempt was made to remove them by treatment with hydrochloric acid, low results for fluorine were invariably obtained. According to Mellor (7), it is possible that the stable fluoborate ion was formed and not completely broken up by the weakly alkaline solutions permissible for the precipitation of calcium fluoride. Whatever the explanation, any appreciable concentration of hydrogen ion resulted in low values for fluorine. Although acetic or other weak acids are suitable for destroying hydroxide and carbonate without causing too high hydrogen-ion concentration, they interfere with the subsequent titration for boron.

The method finally chosen was to destroy the carbonate and alkali by boiling the solution with ammonium chloride. Some trouble was had in the proper coagulation of the precipitate of calcium fluoride, but this was overcome by the use of Fisher "filter accelerators." It was found that calcium fluoride was filterable when these were used, even without the addition of ammonium hydroxide, according to the method of Carrière and Rouanet (2). Coprecipitation of fluoride and carbonate (9) was unnecessary, and has been attacked recently on theoretical grounds by Mougnaud and others (8). Clarke and Bradshaw (3) have shown that the calcium fluoride method can be made to give accurate results by substituting these paper-pulp filter-aids for the coprecipitation and subsequent washing with acetic acid.

The next difficulty occurred through the presence of the excess ammonium chloride in the filtrate containing boron. Ammonium ion causes the end point to appear too late, through buffer action. It was removed by the addition of

strong sodium hydroxide solution and boiling until the vapors ceased to affect litmus paper. The calcium ion in excess from the calcium fluoride precipitation, which partially precipitated as hydroxide, was removed by filtration, the solution transferred to a volumetric flask, and aliquot portions titrated by the standard method, using mannitol (5). Good results were also obtained for boron.

The experimental procedure as finally decided upon was as follows: Approximately half-gram samples were accurately weighed in No. 00 gelatin capsules and placed in the cup of a Parr sulfur bomb of the electrical ignition type, together with a fusion mixture of 10 grams of sodium peroxide, one gram of potassium chlorate, and 0.5 gram of sugar. The bomb was tightly closed, well shaken, and shorted with direct or alternating current of about 20 volts and 8 amperes. For the fusion wire, standard iron wire "for analysis" was used in order not to introduce additional impurities. The bomb was permitted to become quite hot, and then immersed in cool water until it could be handled. The cup was then removed, and the contents dissolved out by placing it on its side in a 400-cc. beaker, covering it with water, and warming gently. After boiling for a few minutes to coagulate the heavy metallic hydroxides from the cup and the fusion wire, the solution was filtered.

Fifteen grams of ammonium chloride were roughly weighed and introduced into the solution, which was boiled until the odor of ammonia no longer persisted (one to two hours). If a new precipitate formed during the boiling, it was filtered out before proceeding.

To the hot solution, 10 cc. of a 2 *N* solution of calcium nitrate were added drop by drop, with stirring. This provided a large excess of calcium ion to depress the solubility of the precipitate. A filter accelerator was dropped in and macerated well, and the boiling was continued for a few minutes. Occasionally it was necessary to add one cc. of approximately 3 *N* ammonium hydroxide to assist in coagulating the precipitate. The solution was cooled in running water until cold, and filtered, using strong suction and a platinum filter cone. The filtrate was reserved for the boron analysis. The volume of wash-water should not exceed 50 cc. The paper containing the precipitate was dried at 110° C. and ignited to constant weight in a platinum crucible over a Fisher burner.

To the filtrate was added sufficient 4 *N* sodium hydroxide to produce a precipitate of calcium hydroxide and carbonate. The solution was then boiled until the vapors

no longer affected red litmus paper, and filtered into a 250-cc. volumetric flask. After being diluted to the mark and mixed thoroughly by shaking, a 50-cc. portion was withdrawn. This was titrated to neutrality with methyl orange, using 0.1 *N* hydrochloric acid. The remainder of the solution was neutralized with an equivalent amount of hydrochloric acid, but no methyl orange was added. The necessary amount of mannitol was added, together with a few drops of phenolphthalein, and the solution titrated to the first faint tinge of pink with 0.1 *N* sodium hydroxide solution (carbonate-free). The buret reading was calculated to boron.

Using this procedure, the following results were obtained:

SAMPLE <i>Gram</i>	CaF ₂ <i>Gram</i>	F	F	ALICQUOT PART	NaOH SOLUTION	B FOUND	B
		FOUND %	CALCD. %	TITRATED	Nor- mality		Amt. used Cc.
METHYL ACETATE BORON TRIFLUORIDE (CH ₃ COOCH ₃ :BF ₃)							
0.5398	0.4446	40.12	40.19	4/5	0.1258	22.59	7.60
0.5057	4/5	0.1258	22.59	7.627
0.3716	0.3100	40.64	40.19	4/5	0.1258	26.20	7.61
0.5861	4/5	0.1258	26.20	7.627
ETHYL ACETATE BORON TRIFLUORIDE (CH ₃ COOC ₂ H ₅ :BF ₃)							
0.4554	0.3404	36.41	36.56	4/5	0.1258	14.40	7.12
0.3442	4/5	0.1258	14.40	6.97
0.4238	0.3189	36.66	36.56	4/5	0.1258	17.60	7.07
MONOAMMONO BORON TRIFLUORIDE (NH ₃ BF ₃)							
0.2540	0.3510	67.32	67.18	4/5	0.1258	18.90	12.66
0.2976	0.4106	67.20	67.18	4/5	0.1258	22.30	12.75

These compounds were freshly made and purified by crystallization or distillation immediately before the analysis. The three are all solids, easy to obtain in a pure condition, and were chosen for that reason.

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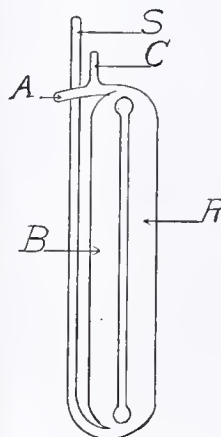
RECEIVED JUNE 3, 1932. From a thesis submitted by Daniel J. Pflaum to the Graduate School of the University of Notre Dame in partial fulfillment of the requirements for the degree of master of science.

A Gas Buret for Catalase Apparatus

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THE buret described is believed to be of some general service as well as being an improvement for the catalase apparatus devised by Appleman (1). This buret was constructed so as to be placed in the water bath for maintaining a constant temperature for the gas to be measured.

The apparatus consists of a short length of buret, a parallel reservoir tube, a siphon which allows the leveling bottle to be operated from without the bath, and connections for the reaction bottle and the outlet. The lower ends of the buret, *B*, and reservoir tube, *R*, are drawn out into tube, *S*, which serves as the apparatus support and forms one arm of the siphon connecting with the leveling bottle. The upper ends of *B* and *R* are drawn out into tube *A*, which connects with the reaction bottle. Tube *A* is also provided with an outlet tube, *C*. The buret with its reservoir tube is calibrated in



centimeters for the readings on the buret. This apparatus permits all the chambers containing gas to be submerged in water. It must be kept in mind that as the buret is shortened and the volume of the reservoir is increased, the errors of reading are increased in proportion.

This arrangement has been in service for one year with good results.

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RECEIVED August 2, 1932.

Large-Capacity Soxhlet Extractor and Reflux Condenser

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THE need for a device of large capacity which would serve for the extraction of considerable quantities of solid material led the author to design a modification of the Soxhlet extractor. The extractor described here, shown in detail in Figure 1, is rugged in design and construction and is not particularly difficult to make. The most

convenient starting point seemed to be a 5-liter Pyrex balloon flask. Larger flasks would involve such quantities of solvent that it seemed more desirable to build a battery of 5-liter extractors rather than to make larger ones.

The stem, *A*, which carries the vapor to the condenser, is made of tubing having an outside diameter of 30 to 35 mm. and contains the siphon tube, *B*, which is made of 8-mm. tubing. To insure certain siphoning, the bend at the top of the siphon tube is allowed to flatten somewhat and the opening where the lower end is sealed through the stem is allowed to constrict until it is about 3 mm. in diameter. Thorough annealing of the extractor is necessary.

The stem can be lined up in the middle of the flask and the

reflux condenser, *D*, offset somewhat, as shown, to return the condensate to the extractor. It is preferable that these extractors be supported by a large ring rather than by a clamp around the neck. They may be fitted with ground-glass joints if desired. The joints need not be larger than those used with the customary small Soxhlets. In order to prevent clogging of the siphon, if the solid being extracted has a tendency to crumble, a layer of glass beads covered with cotton may be used as a support in the bottom of the flask.

The problem of securing sufficient condensate from a reflux condenser to make extractors of this size useful led the author to develop what he believes to be a novel condenser. The

proper design of a large-capacity reflux should take several factors into account. It is preferable that the condensate not be returned down the tube, which is carrying vapor to the cooling surface, for with high vapor velocities, choking will occur. It would be desirable to avoid passing vapor over portions of the condensing surface which are already working at capacity, and the vapor should have only a short way to go before reaching the condensing surface. To secure these desired features, the use of a straight or bulbed tube of large diameter is not of itself desirable. The condenser must be efficient in operation, simple in design, and rugged in construction if it is to be practical for laboratory use.

The condenser is shown in Figure 2. A large tube, *A*, 25 to 30 mm. inside diameter thin-wall Pyrex, is used for the inner tube. Up the center of this passes another tube, *B*, 10 mm. smaller, which is sealed off at the upper end and is perforated with two vertical, diametrically opposite, rows of holes 8 to 10 mm. in diameter and spaced 18 to 20 mm. apart, measured from center to center. The vapor is directed against the condensing surface from these ports, and their arrangement in vertical rows allows uninterrupted flow of condensate down part of the condenser wall. The condensate is returned to the flask from sump *D* through a 6-mm. tube, *E*, sealed in as shown in the sketch.

Three glass guide-pins, *F*, sealed to the manifold, *B*, are fitted by filing the ends before the manifold is sealed in at *G*. They provide the support necessary to prevent breakage due to rough handling, and yet allow the manifold to expand when hot vapor passes through it.

The inner tube of the condenser is constricted 2 to 3 cm. above the end of the manifold, giving room for a safety bulb, *H*, about 6 to 8 cm. long, which will take care of surges when the condenser is working at capacity. It is advantageous to bend the water inlet and outlet downward as shown and to have an enlargement, *I*, in the nose of the condenser to rest upon the stopper.

The approximate dimensions of the condensers which the author has constructed are as follows: length of jacket and condensing surface, 60 to 70 cm.; over-all length, 90 cm.; length of nose of condenser, 20 cm. Condensers of these dimensions have a capacity of 8 to 10 liters of acetone per hour with cooling water temperature of 7° C. They will not reach capacity with alcohol or acetone in a 5-liter

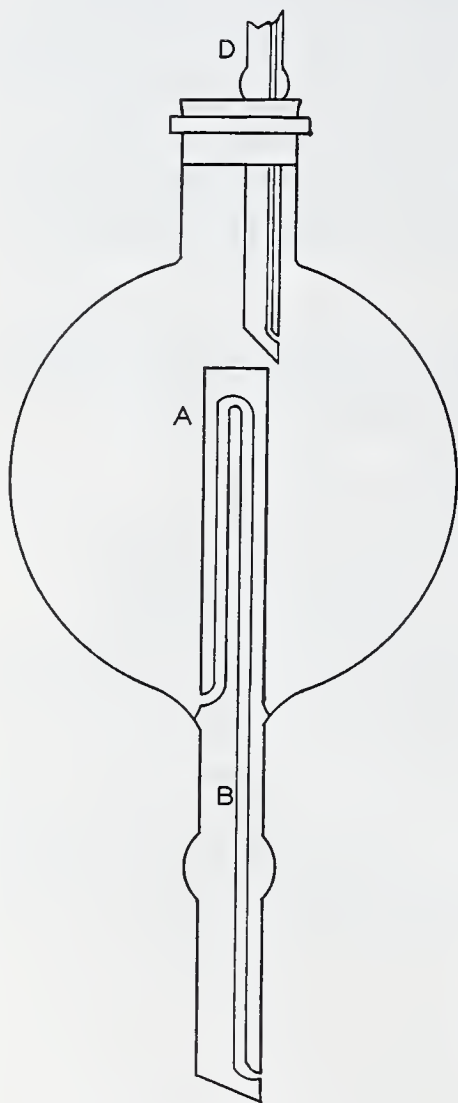


FIGURE 1

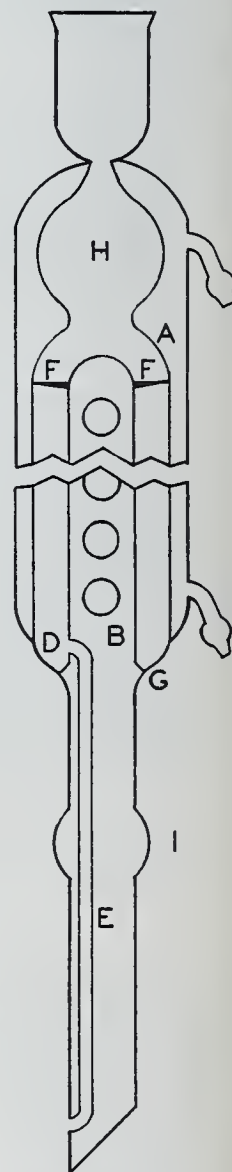


FIGURE 2

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flask heated on a steam bath. The capacity for ether is surprising, and only a faint odor can be detected at the top. Since condensation is favored by a film of cold liquid running down the inner tube, the condenser has not reached capacity when the vapor is condensing clear to the top of the manifold.

ACKNOWLEDGMENT

The author wishes to acknowledge the valuable assistance of Milton E. Ryberg, also of the University of Minnesota, in the construction of the extractors.

RECEIVED April 29, 1932.

Specific Test for Orange Honey

R. E. LOTHROP, Bureau of Chemistry and Soils, Washington, D. C.

OWING to its pleasant flavor, orange honey is generally considered to be one of the most desirable floral types for table use. In California orange is one of the important sources of honey. The trees bloom in April, and the flow of nectar is extremely abundant, at times being secreted in such quantities that men working in the orchards are saturated with it. The flow lasts about three weeks, and during this time strong colonies of bees usually average 60 or more pounds of orange honey per colony. One case is recorded in which more than 170 pounds of orange honey were stored by a single colony of bees in 10 days.

The honey from orange is white in color, heavy in body, of the finest quality, and is much in demand in the markets. This has created an incentive for some unscrupulous honey dealers to attempt the marketing of honey labeled "orange" in which some less expensive light colored honey is substituted for part of the orange. In some cases honey is sold as orange honey which contains very little orange or none at all. The writer recently secured a sample of honey being sold in California as orange that proved from examination of the pollen¹ to consist chiefly of Hawaiian algaroba honey. Although microscopic examination of the pollen was effective for determining the floral source of the honey in this particular case, this method cannot be relied on for determining the floral source with reasonable certainty in all cases. As pointed out by Nelson (1), the distinctive pleasant aroma of orange honey is due to the presence of methyl anthranilate. Methyl anthranilate, or the methyl ester of *o*-amidobenzoic acid, $C_6H_4(NH_2)(COOCH_3)$, is rather widely distributed in nature. It occurs as a constituent of oil of orange flowers, to which it imparts the characteristic aroma. It also occurs in a number of other fragrant oils in small amounts. A test for detecting methyl anthranilate in fruit juices in quantities as small as 0.1 mg. has been devised by Power (2).

In order to determine whether or not detectable quantities of methyl anthranilate are present in other floral types of honey besides orange, tests for methyl anthranilate were conducted on a considerable number of representative floral honeys, special attention being given to those which constitute the main source of honey produced in California. The test for methyl anthranilate, essentially that described by Power, was carried out as follows:

One kilogram of the honey to be tested is dissolved in 600 to 800 cc. of distilled water, and the resulting solution distilled in a current of steam until about 700 cc. of distillate are collected. The distillate is extracted with three successive portions of chloroform of 35 cc. each, the united chloroform liquids are passed through a dry filter and carefully evaporated in a small beaker on a water bath, a current of air being passed over the surface until the solvent is just completely removed. The residue is then immediately treated with 2 cc. of 10 per

cent sulfuric acid, and the solution is transferred to a test tube, when it is ready for the specific test. (If a residue obtained by the evaporation of the chloroform is kept for any length of time exposed to the air before treatment with the dilute acid, volatilization of the ester will occur.) The acid liquid is cooled, one drop of a 5 per cent solution of sodium nitrite is added, and subsequently a few crystals of urea are added in order to destroy any possible excess of nitrous acid.

The diazotized liquid is now added to a mixture consisting of one cc. of 0.5 per cent pure β -naphthol (prepared by dissolving 0.5 gram of pure β -naphthol in 2 cc. of 10 per cent sodium hydroxide, and diluting to 100 cc.), one cc. of 10 per cent sodium hydroxide, and one cc. of 10 per cent monohydrated sodium carbonate. If not less than 0.0001 gram of methyl anthranilate is present, a yellowish red precipitate will be produced.

TABLE I. RESULTS OF TESTS FOR METHYL ANTHRANILATE IN HONEYS OF VARIOUS FLORAL TYPES

PREDOMINANT FLORAL SOURCE ^a	ORIGIN	QUANTITY DISTILLED Grams	RESULTS OF TEST
Algaroba	Hawaiian Islands	1000	Negative
Sage	California	1000	Negative
Alfalfa	California	1000	Negative
Holly	California	1000	Negative
Manzanita	California	1000	Negative
Tarweed	California	1000	Negative
Eucalyptus	California	1000	Negative
Sumac	Connecticut	1000	Negative
Cotton	Texas	1000	Negative
White clover	Ohio	1000	Negative
Buckwheat	Ohio	1000	Negative
Tulip poplar	Maryland	1000	Negative
Tupelo	Florida	1000	Negative
Palmetto	Florida	1000	Negative
Orange	Florida	500	Strong positive test
Calif. orange 1	California	500	Strong positive test
Calif. orange 2	California	1000	Strong positive test (heavy orange-red ppt.)
Mixture: 50% orange and 50% tulip poplar	1000	Strong positive test
Mixture: 25% orange and 75% tulip poplar	1000	Strong positive test
Mixture: 10% orange and 90% tulip poplar	1000	Positive
Mixture: 5% orange and 95% tulip poplar	1000	Negative

^a Considerable care was taken to procure samples that truly represented floral types given. Each sample was obtained from a reliable dealer in a region which is known to produce that particular kind of honey, and at a time of year when honey is ordinarily extracted. Floral types were checked by careful notation of physical properties, such as flavor and aroma, color, and granulation properties, and a comprehensive chemical analysis of each was made. In addition, pollen of each sample was examined to obtain confirmatory data relative to floral source.

The results obtained by application of the test described above to honeys of various floral sources are given in Table I. From the results it is seen that, of the honeys tested, only orange responded positively to the test. Apparently methyl anthranilate is a flavoring compound peculiar to orange honey, not occurring in other floral types, at least in amounts that can be detected by this test. Its detection in honey, therefore, serves as a specific test for orange honey. By using

¹ The examination of the pollen of this sample was carried out by G. L. Keenan, microanalyst of the Food and Drug Administration, U. S. Department of Agriculture.

one-kg. portions of honey for distillation, it is possible to detect as little as 10 per cent orange in a mixed honey. The distillation of quantities greater than one kg. would make it possible to detect less than 10 per cent orange in a mixed honey. A one-kg. portion is used, as it represents the largest amount that can be conveniently distilled with ordinary laboratory equipment.

Since pure orange honey can usually be recognized by its characteristic flavor, it might seem superfluous to resort to chemical tests as a means for detecting it. The test described is easy to carry out, however, and might be particularly useful

for detecting the presence of orange in mixed or blended honey. In addition, it eliminates the personal equation involved in an organoleptic test (based on gustatory senses). The method might also be used to obtain a rough estimate of the relative amount of orange present in a blended honey.

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RECEIVED June 15, 1932. Contribution 125 from the Carbohydrate Division, Bureau of Chemistry and Soils, U. S. Department of Agriculture.

Determination of Arsenic

Iodometric Acidimetric Method

R. C. Wiley, J. P. Bewley, AND R. IREY, University of Maryland, College Park, Md.

ARSENIC readily forms volatile compounds. A very common method for determining arsenic is by distilling it as arsenious chloride. Attempts have also been made to determine arsenic by converting it to arsine and absorbing the arsine in some standard solution.

Lochman (2) determined arsenic qualitatively by passing the arsine formed through mercuric chloride solution. Ericsson (1) conducted arsine through 0.1 *N* silver nitrate and precipitated the silver with hydrochloric acid. The arsenic was then titrated with 0.002 *N* iodine. Many other methods have been devised for measuring arsine by passing it through standard solutions. The well-known Gutzeit method is, of course, a colorimetric means of measuring arsine.

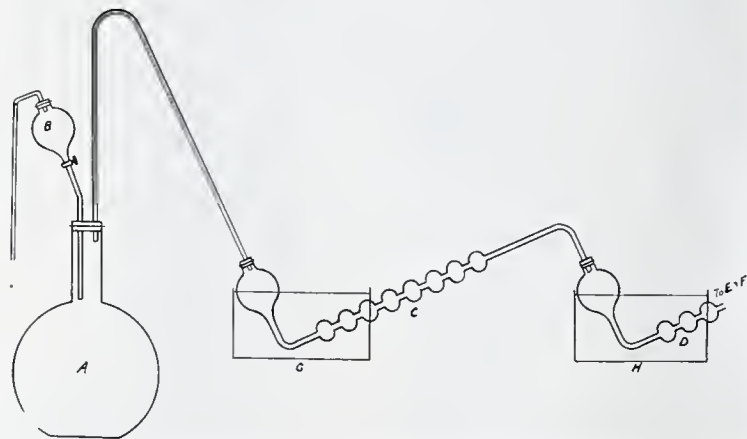


FIGURE 1. DIAGRAM OF APPARATUS

The basis for the method described here is, first, conversion of the arsenic to arsine, and next absorption of the arsine by a standard iodine solution. This is followed by the titration of the residual iodine and the titration of the acids formed in the oxidation.

For this investigation the following solutions were prepared:

0.1 <i>N</i> I	0.01 <i>N</i> As ₂ O ₃
0.1 <i>N</i> Na ₂ S ₂ O ₃	0.01 <i>N</i> Na ₂ S ₂ O ₃
0.1 <i>N</i> NaOH	
0.1 <i>N</i> As ₂ O ₃	

In addition, arsenic-free sulfuric acid and zinc were used. All solutions were carefully standardized and the zinc and sulfuric acid were found nearly free of arsenic by the Gutzeit test. A blank was run on all reagents.

All rubber tubing and stoppers used were first boiled in a solution of sodium hydroxide, washed, and boiled in dilute hydrochloric acid. They were then soaked overnight in water.

PROCEDURE

The solution of the sample, in which the arsine must be in the arsenious state, is placed in the flask and about 10 grams of 20-mesh zinc are added. The volume of the solution should not be more than 20 to 30 cc. The stopper is now placed in the flask and a measured amount of standard iodine solution distributed through the Meyer bulb tubes, *C* and *D* of Figure 1, with sufficient water to bring the volume in each tube to about 75 cc. The bulb tube, *E*, which is not shown, contains a 1 per cent solution of potassium iodide to dissolve any iodine vapor from *D*. As a further precaution, another bulb tube, *F*, is connected to *E* and is filled with water. On rare occasions *F* is found useful. A piece of mercuric chloride paper is inserted in *F* to indicate any escaping arsine. The tubes, *G* and *H*, should be filled with cold water.

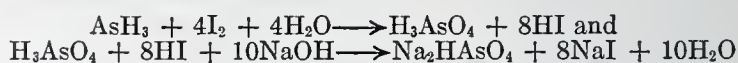
The separatory funnel, *B*, is now filled with 75 per cent sulfuric acid and about 5 cc. are allowed to run into *A*. The acid is added in 10-cc. portions at about 10-minute intervals for about 40 minutes. At the end of this time most of the zinc will be dissolved. The contents of the flask are then heated to gentle boiling for about 5 minutes. The solution in *C*, however, should not become warm. The contents of *C*, *D*, *E*, and *F* are then washed into a beaker and titrated with standard sodium thiosulfate using starch for an indicator.

After the titration with thiosulfate, one of the following procedures was adopted:

1. When a large amount (more than 0.05 to 0.07 gram of arsenious oxide) of arsenic was present, the solution was neutralized with sodium bicarbonate and titrated back with standard iodine.
2. When a small amount (less than 0.05 to 0.07 gram of arsenious oxide) of arsenic was present, the solution was titrated with standard sodium hydroxide, using phenolphthalein as indicator.

DISCUSSION

In method 2, when the arsine is completely oxidized, the following reaction takes place:



It will thus be seen that 1 cc. of 0.1 *N* iodine is equivalent to 0.001237 gram of arsenious oxide, and 1 cc. of 0.1 *N* sodium hydroxide is equivalent to 0.0009896 gram of arsenious oxide.

The above reaction between arsine and iodine goes to completion when the arsine generated from not more than 0.05 to

0.07 gram of arsenious oxide is passed into 100 cc. of 0.05 *N* solution of iodine. The determination should be arranged so that not more than this amount of arsenic is present if it is desired to titrate both the residual iodine and acid formed.

TABLE I. ARSENIOS OXIDE FOUND AND PRESENT BY IODOMETRIC AND ACIDIMETRIC METHODS

SAMPLE	As ₂ O ₃ BY IODOMETRIC METHOD			As ₂ O ₃ BY ACIDIMETRIC METHOD		
	Present	Found	Diff.	Present	Found	Diff.
	Gram	Gram	Gram	Gram	Gram	Gram
I	0.02475	0.02461	-0.00014	0.02475	0.02475	0.00000
II	0.02475	0.02480	+0.00005	0.02475	0.02493	+0.00018
III	0.02475	0.02492	+0.00017	0.02475	0.02458	-0.00017
IV	0.02475	0.02477	+0.00002	0.02475	0.02459	-0.00016
V	0.02475	0.02492	+0.00017	0.02475	0.02464	-0.00011
VI	0.02475	0.02480	+0.00005	0.02475	0.02483	+0.00008
VII	0.02475	0.02475	0.00000	0.02475	0.02464	-0.00011
VIII	0.002475	0.002596	+0.00012	0.002475	0.00282	+0.00033
IX	0.04950	0.04941	-0.00009	0.04950	0.04928	-0.00022
X	0.04950	0.04979	+0.00029	0.04950	0.04948	-0.00002
XI	0.04950	0.04954	+0.00004	0.04950	0.04948	-0.00002
XII	0.04950	0.04964	+0.00014	0.04950	0.04928	-0.00022

TABLE II. RESULTS OBTAINED BY PROCEDURE 1 WITH ARSENATES AND ARSENITES PRESENT IN RECEIVING IODINE SOLUTION

SAMPLE	As ₂ O ₃ PRESENT	As ₂ O ₃ FOUND	DIFFERENCE
	Gram	Gram	Gram
1	0.09893	0.10019	+0.00116
2	0.09893	0.09809	-0.00084
3	0.09893	0.09840	-0.00053
4	0.09893	0.09842	-0.00051
5	0.09893	0.09809	-0.00084
6	0.08000	0.08032	+0.00032
7	0.12000	0.11976	-0.00024
8	0.10000	0.09987	-0.00013

When larger than the above-mentioned amounts of arsenic are present in the sample, the receiving iodine solution will contain both arsenate and arsenite. In such cases, the volume of iodine originally added and the amount used in back titration are added, and from this is subtracted the volume of thiosulfate used in titration. The arsenic present is found by multiplying the difference by the proper factor. For example, suppose 120 cc. of 0.1 *N* iodine were used as the receiving solution and 30 cc. of 0.1 *N* thiosulfate were used to titrate the residual iodine, and also that 7 cc. of 0.1 *N* iodine were used to titrate back after neutralization.

0.1 <i>N</i> I, cc.	120
0.1 <i>N</i> Na ₂ S ₂ O ₃ , cc.	30
	90
0.1 <i>N</i> I used in back titration, cc.	7
	97
97 × 0.001237 = 0.119989 gram As ₂ O ₃ present	

Tables I and II show results obtained.

COMMENTS

Since in going from arsine to orthoarsenic acid arsenic changes 8 in valence, it is possible to determine very small quantities of arsenic in a volumetric way. It has been found practical to use 0.01 *N* solution of iodine, one cc. of which equals 0.0001237 gram of arsenious oxide. Since one can check readily to about 0.2 cc., it has been found possible to determine quantities of arsenic as small as 0.00002 gram. The method herein described should be four times as sensitive as the ordinary titration of arsenic with iodine.

The acidimetric titration is a valuable check on the accuracy of the iodometric titration.

The work done shows that it is impossible to liberate all the arsenic from a sample as arsine without boiling. The boiling has gone far enough when the last particle of metal has been dissolved. Although the reaction of the acid on the material in the flask may have ceased before boiling, it will be found that when the contents of the flask are brought to boiling par-

ticles of dark-colored material will dissolve. No doubt arsine is also dissolved in the liquid in the flask, and this is liberated upon boiling.

Sufficient standard iodine solution should be present in tubes *C* and *D* so that all of it is not reduced by the arsine, else unreliable results will be obtained.

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RECEIVED June 23, 1932.

A Laboratory Extractor

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THE accompanying photograph shows an extractor of considerable capacity which was constructed almost entirely by the assembly of common laboratory apparatus. Within a tall-form liter beaker was placed a glass tripod which was readily constructed of glass rod. A 35 by 70 mm. crystallizing dish rested in an inclined position on this tripod. A 15-cm. folded filter within this dish contained the material to be extracted. Suspended in the mouth of the beaker was a 250-cc. distilling flask which served as the condenser.

The extractor is particularly well adapted to the purification of organic compounds. It resembles in some respects an extractor described in the literature (1), wherein a large funnel is used to support the filter. It has numerous advantages, however, over the "funnel" extractor. Comparative tests showed that it has a much higher speed of extraction; the solvent is condensed more effectively when boiled vigorously; the drip from the condenser flask does not channel through the charge in the filter; "choking" of ascending vapor with condensate in the funnel stem is avoided; and contamination by material from stoppers does not occur.

When used with 200 cc. of carbon tetrachloride as the extraction medium, no appreciable amount of solvent escaped during a 6-hour run. Decolorizing charcoal, intimately mixed with the material to be extracted prior to filling up the filter, frequently assisted purification.

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RECEIVED June 21, 1932. Contribution 102 from the Experimental Station, E. I. du Pont de Nemours & Co.



Practical Vacuum-Tube Potentiometer for pH Measurement with Glass Electrodes

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THE instrument to be described is the result of a series of trials and experiments growing out of a demand in this department for a satisfactory means of determining the pH of intestinal contents. The glass electrode has been shown by McInnes and Dole (5) to develop potentials directly proportionate to pH even in the presence of substances which interfere seriously with pH measurements by other electrometric means, and therefore to promise greater accuracy than other methods. The high resistance of the glass membrane has, however, by necessitating the use of a very sensitive electrostatic device for measuring the potential, proved a serious obstacle to the development of a satisfactory instrument.

Because of this high resistance, it is obviously not possible to balance the potential against that of a potentiometer directly. The Compton electrometer, as employed by McInnes, has apparently been found unsatisfactory by other workers. Several attempts have been made to construct

An easily operated vacuum-tube potentiometer for pH measurements is described. Use is made of a low grid-current, low plate-voltage tube now available for this work. Galvanometer drift has been reduced to a negligible minimum by automatic compensation for filament voltage changes, and "floating" of filament battery on a charging source. Suggestions for a shielded thermostat box and a high-insulation vacuum-tube switch are given. One galvanometer is used for both potentiometer standardization and as a plate-current indicator, working as a null instrument in both functions.

a potentiometer on the vacuum-tube principle (2, 9, 10) but inability to control grid-current fluctuations arising from leakage or electrostatic charges, and those of the various battery voltages, has been a source of great annoyance in the operation of these instruments.

A four-element, low grid-current, low anode-potential vacuum tube recently put on the market¹ (3, 4, 6), and the incorporation of a number of new features of construction and assembly, have now

eliminated this source of trouble. The present instrument has the additional decided advantage of relative simplicity of operation.

The principles (7, 8, 11) upon which this instrument operates will be clear from a study of the vacuum-tube circuit, shown in Figure 1. For any given grid voltage, all other conditions being maintained constant, the anode current, as indicated by a galvanometer, will assume a specific value. Insertion in the grid circuit of an additional voltage, that of the electrode system, causes the anode current to

change, but upon opposing an equal voltage from the potentiometer, the anode current resumes its original value. The system used differs from that of Dubois (2) in that no attempt is made to work the tube at its floating grid potential, where the grid current is zero. With suitable precautions, the FP-54 tube can be made to have a grid current of 10^{-15} amperes or less, which is low enough to preclude appreciable polarization effects.

Anode current drifts due to filament- and grid-battery fluctuations have been reduced to a negligible minimum in two ways. Part of the voltage drop across the filament is utilized to supply a current which is passed through the galvanometer in opposition to the normal anode current (1). This method not only has the advantage of allowing the galvanometer to be operated from its true zero, but also

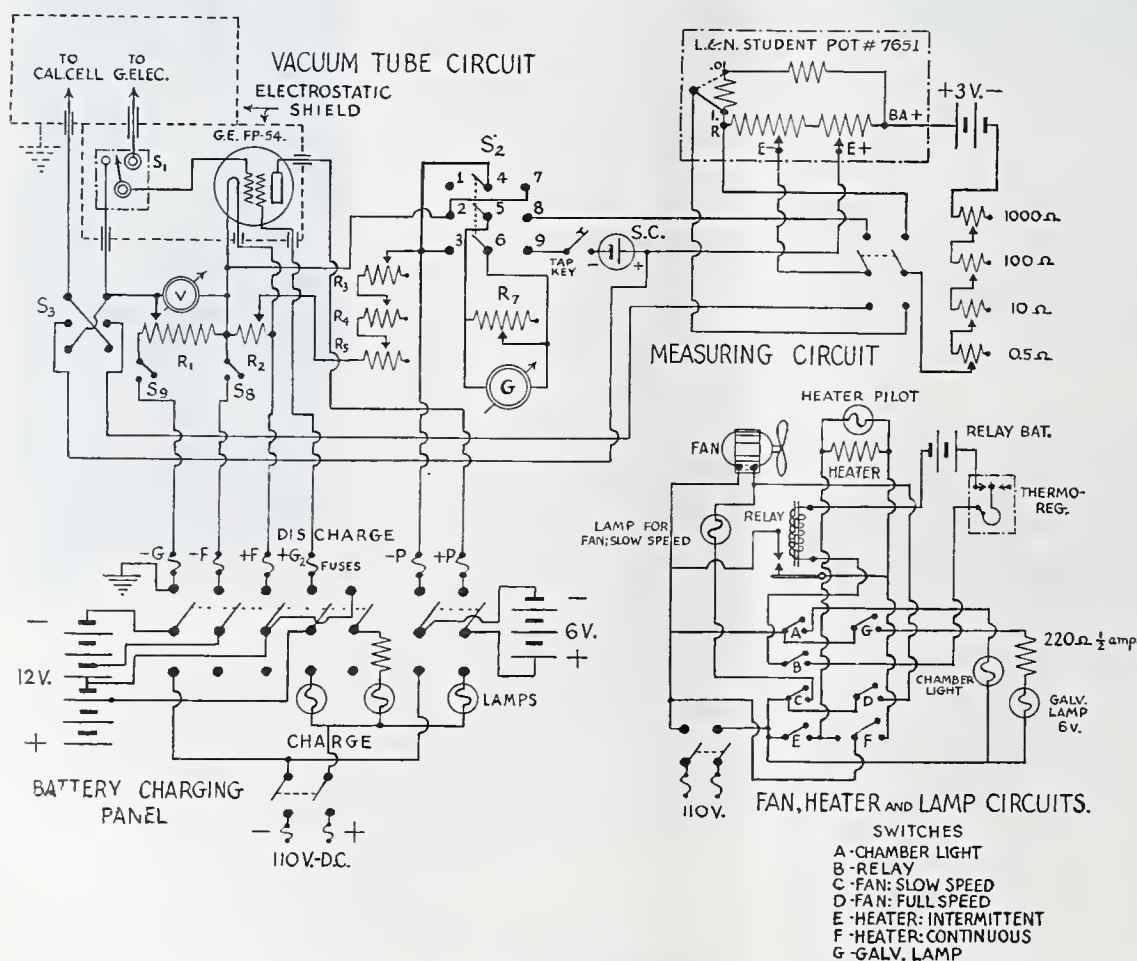


FIGURE 1. WIRING CIRCUITS FOR COMPLETE GLASS ELECTRODE SET-UP

¹ General Electric FP-54.

automatically compensates for filament-battery fluctuations; a rise in filament voltage causes increased electron flow and hence a rise in anode current, but the counteracting current increases simultaneously, thus preventing a change in galvanometer deflection. In addition, large filament-battery fluctuations have been circumvented by floating this and the grid battery during use on a direct current charging source through a resistance of appropriate size so that the charging current will be slightly less than that of the load.

CONSTRUCTION

ELECTRICAL. A three-pole double-throw switch, S_2 in Figure 1, allows the galvanometer to be used in standardizing the potentiometer as well as in the tube plate circuit. The contacts 4 and 7 prevent the interruption of plate current when the galvanometer is being used for standardization. Switch S_3 reverses the potentiometer polarity for measuring solutions of low pH. Resistance R_1 provides a means of varying the grid voltage, which is indicated by a small panel voltmeter of proper range. R_7 is the galvanometer protective and damping shunt, which consists of a series of resistors connected to the studs of a rotary switch. The values of these resistors for use with the L. & N. type 2500-e galvanometer

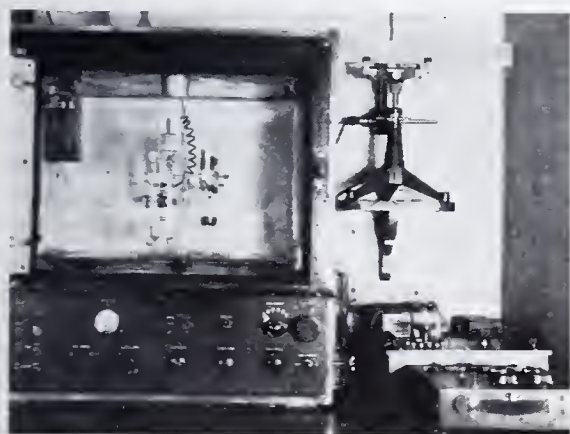


FIGURE 2. INSIDE OF CHAMBER SHOWING ELECTRODE SYSTEM

are 10, 100, 500, 1000, and 500 ohms, which give convenient steps of galvanometer sensitivity with good damping characteristic. A view of the inside of the chamber showing the electrode system is given in Figure 2.

MECHANICAL. It is necessary to enclose the entire assembly, with the exception of the potentiometer, galvanome-

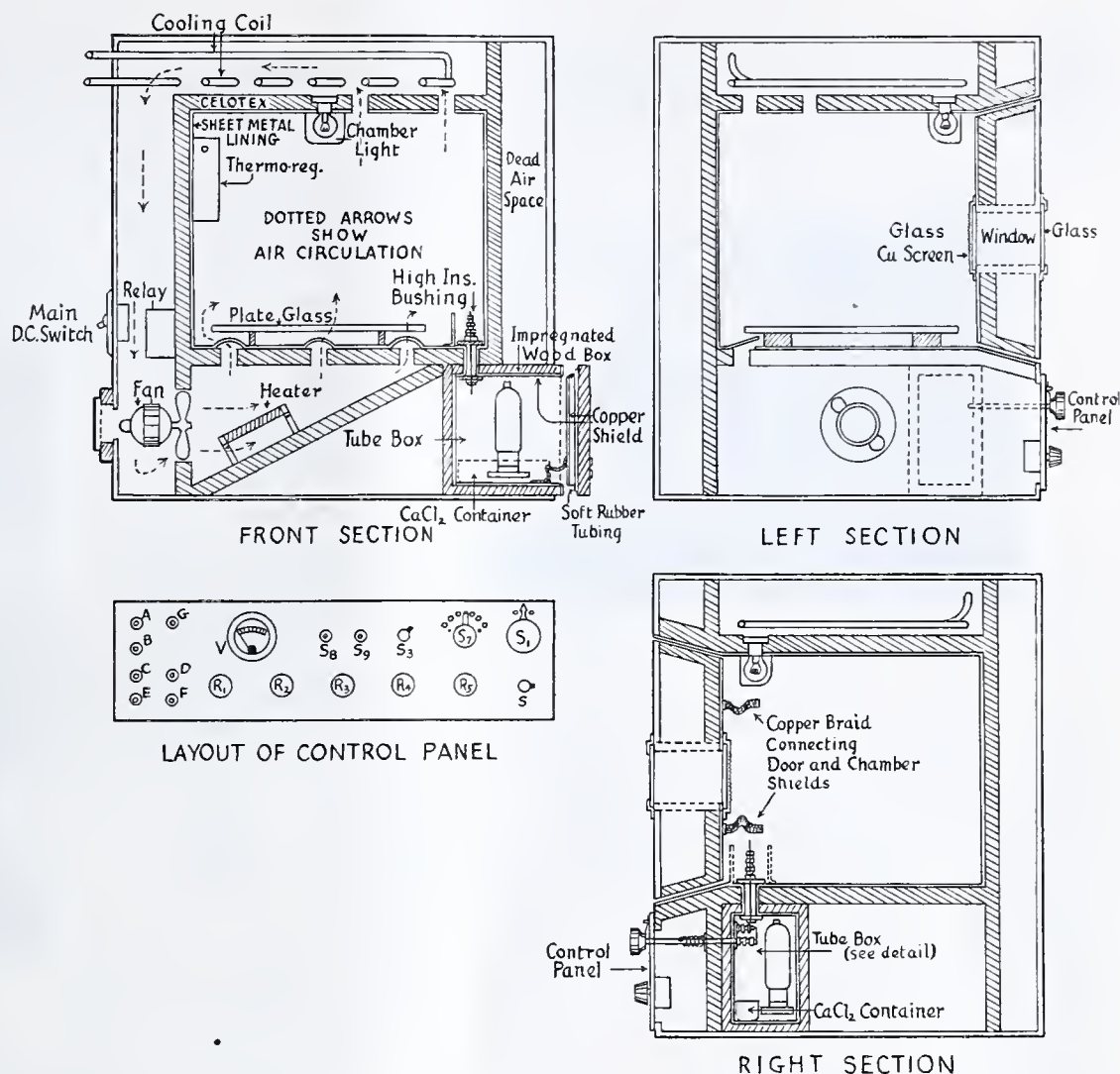


FIGURE 3. CONSTRUCTION OF THERMOSTAT BOX

ter, batteries, and associated apparatus, in an electrically shielded box arranged to maintain constant temperature. A thermoregulator within the main chamber operates a heating resistance (Electrad 200 ohms-75 watts) through a small relay whose coil is energized by one or two dry cells. A thermometer placed in the test solution or in some other convenient place may be observed through the gauze-shielded window and illuminated with a small candelabra-base 110-volt lamp operated by a switch on the front panel. The connections for this light and for the air-conditioning system are shown in Figure 1. Diagrams showing the box constructed by the author, which is a modification of one used by Dubois, are given as a suggestion (Figure 3). The vacuum tube and switch S_1 are housed in a separate wooden box, lined inside with sheet copper and impregnated against air and moisture with hot wax or pitch; this box is built into a corner of the thermostat box. Its shield and that of the main chamber are to be thoroughly grounded. An arrangement of the apparatus with a good view of the tube box is shown in Figure 4. Details of the high-insulation switch, S_1 , bushings, and connections, are shown in Figure 5. Much depends upon the insulating qualities of this switch so that careful thought should be given to its construction and placement. Three six-volt 100 ampere-hour storage batteries are recommended for use with this instrument. Figure 6 shows a complete set-up.

OPERATION

The potentiometer is standardized in the usual way, making use of the galvanometer switch, S_2 . As balance is approached, the galvanometer shunt is moved toward the

higher resistance studs, final adjustment of potentiometer battery current being made with the shunt set on the last stud. After standardization is completed, the shunt is thrown back and the same step-by-step technic followed for all

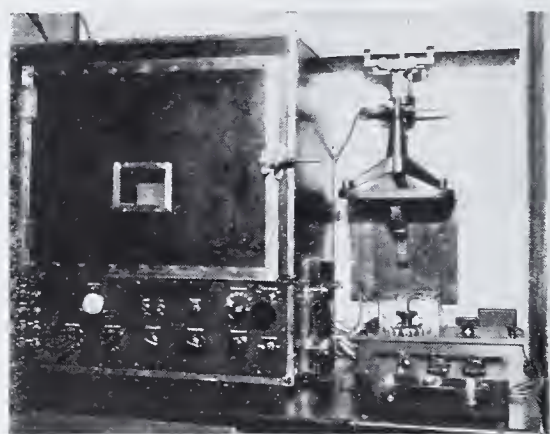


FIGURE 4. VIEW OF TUBE BOX

further operations. Switch S_2 is then thrown so as to connect the galvanometer to the anode circuit (e. m. f. position), and with the high-insulation switch, S_1 , on stud 2, which connects the grid of the tube directly to the working grid voltage, the galvanometer is brought to zero, by means of the resistances R_2 , R_3 , R_4 , and R_5 . Switch S_1 is then thrown to stud 1 so as to include the electrode system and the potentiometer measuring circuit, and the latter is adjusted until the galvanometer deflection returns to zero. If the deflection increases when the potentiometer setting is increased from zero volts, the potentiometer polarity should be reversed with switch S_3 . At balance it is possible to throw switch S_1 back and forth without causing a deflection of the galvanometer, and this provides a check on the accuracy of the potentiometer setting, which, at zero galvanometer deflection, is the e. m. f. of the electrode system.

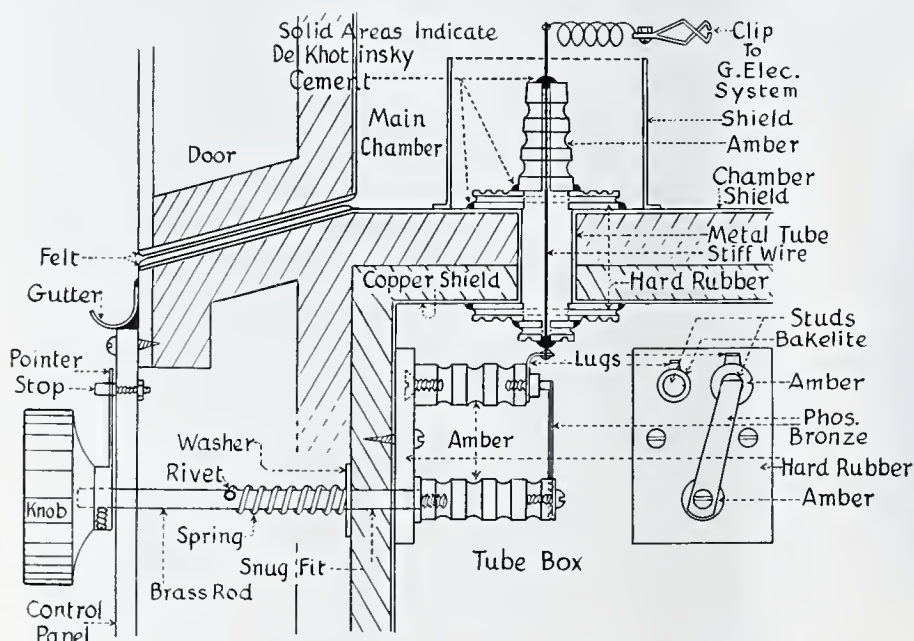


FIGURE 5. DETAILS OF HIGH INSULATION SWITCH AND BUSHINGS

In measuring grid current, a high resistance (100 megohms or more) of known value is substituted for the electrode system and the procedure as given above is followed. The voltage as read on the potentiometer and the known resistance are applied in Ohm's law.

CALCULATION OF pH

It has been observed that the asymmetry potential of the glass membrane, so-called by McInnes and Dole (5), often does not remain constant. This has been found to be especially true with a new glass cell; after a period of use it assumes a constant value. It is advisable, when first setting up the instrument, to test a batch of glass cells for potential drift, and to select one which shows relatively little. After some days readings obtained with this membrane will be found nearly constant for a single solution, showing no appreciable drift from hour to hour, and only small changes from day to day. During this period pH calculations may be made satisfactorily by reference to a standard of known pH, the relation being

$$\text{pH}_g = \text{pH}_s = \frac{E_s - E_g}{0.0591} \text{ at } 25^\circ \text{C.}$$

where E represents potential, g the unknown solution, and s the standard. After the glass membrane attains a constant asymmetry potential, the use of a standard is necessary only to check this fact from day to day; pH may then be calculated by the use of an empirical formula involving the combined constants, x in the following equation, for glass, silver, and calomel electrodes, as determined for a given set-up with solutions of known pH:

$$\text{pH} = \frac{E_g - x}{0.0591} \text{ at } 25^\circ \text{C.}$$

Precision in measurement will depend to some extent upon the galvanometer and potentiometer employed. Numerous repeated tests have shown that the presence of the vacuum tube does not introduce errors of any kind in this set-up. Even before the asymmetry potential of the glass membrane becomes constant, measurements are easily attainable to within ± 0.03 pH; with a constant and carefully calibrated instrument the average error is reducible to the third decimal place.

Besides its usefulness in pH measurement, many other applications involving determination of e. m. f. might be suggested for this instrument.

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FIGURE 6. COMPLETE SET-UP

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Determination of Metals in Organic Combination

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AS POINTED out in the report of the Sub-Committee on Synthetic Organic Chemicals of the American Drug Manufacturers Association, "organic compounds of mercury are assuming an ever increasing importance in medicine as antiseptics, anti-syphilitics, and diuretics." During the year 1930, ten selected methods for the analysis of organic mercury compounds were studied in five different laboratories under the supervision of this committee. Variations of surprising magnitude were found to occur. Using the same method for a given compound, differences as great as 2 or 3 per cent were noted. The results for a different mercurial by different methods show even greater variation, being as much as 7 per cent in the cases of mercury salicylate and mercurochrome. About this time, during the course of a study of certain synthetic organo-metallic compounds in this laboratory, it became very desirable to secure a more rapid method of metal analysis.

Experience in the foregoing analyses suggested strongly that greatest progress could be made by devising a simpler and more satisfactory mode of decomposing the organic compound than the sulfuric acid-permanganate, sulfuric-nitric acid, hydrochloric acid, perchloric acid, and persulfate mixtures commonly employed in the past. This was found in the use of fuming sulfuric acid and 30 per cent hydrogen peroxide (Superoxol). The fuming acid (15 per cent SO_3) dissolved the organic compounds either in the cold or on gentle warming, facilitating complete oxidation, and the excess hydrogen peroxide on spontaneous decomposition left no residue of inorganic salts. With nearly all of the compounds studied, oxidation was found to be complete within 3 to 5 minutes, giving a water-white solution containing only sulfuric acid and the metal as sulfate.

The use of hydrogen peroxide for hastening decomposition during Kjeldahl digestions was first suggested by Kleeman (5) in 1921, and has subsequently found application in biological assays (6, 7, 12). Oakdale and Powers (9) have employed it as a secondary oxidizing agent in a new method of halogen determination.

Since the completion of most of the following work, the authors have found that Graham (2) employed a sulfuric-peroxide mixture of the decomposition of mercurial insecticide samples, and Schulek and Villecz (10) have utilized it in the determination of arsenic. These methods do not, however, seem to be well known in this country, and to the best of our

A study has been made of the action of fuming sulfuric acid and 30 per cent hydrogen peroxide upon organo-metallic compounds containing mercury, arsenic, antimony, bismuth, gold, silver, and germanium. Decomposition of all organic matter is rapid and complete, leaving a solution containing only the metal, usually as sulfate. To this solution, customary methods of analysis may be readily applied; precipitation as sulfide has been found useful particularly in the cases of mercury, antimony, bismuth, and germanium, as has a modification of the Neuberry method in the case of arsenic.

knowledge perhydrol-sulfuric acid decomposition has not been applied to the systematic decomposition of organo-metallic compounds.

MERCURY

Several methods were studied for the completion of the analysis in each instance. In the absence of halogen, dilution with water and titration of mercury with potassium sulfocyanate in the presence of nitric acid was found to be satisfactory and apparently accurate.

Where speed is important, this technic has many advantages, enabling the complete analysis to be carried out in 15 to 30 minutes. Precipitation by Jamieson's reagent and either titration with potassium iodate or weighing as mercury zinc sulfocyanate (3) were looked upon with favor until, in the case of mercury salicylate, the titration gave low and inconsistent results; the reason for this has not been found.

Since the chief aim of this study was the elaboration of a method applicable with equal accuracy to all types of organic mercurials, with and without halogens, precipitation as sulfide seemed to offer the greatest possibilities.

It was found that the oxidation mixture, after dilution and cooling, could be precipitated directly by hydrogen sulfide; in the absence of inorganic salts, the authors not only failed to observe the inaccuracies reported by Fenimore and Wagner (1), but found that precipitation was complete within 15 minutes. No formation of sulfur was observed. If the precipitate was washed successively with alcohol, carbon disulfide, and ether, drying was complete in 20 minutes at 105° C.

PROCEDURE IN ABSENCE OF IODINE. The sample containing approximately 0.1 gram of mercury is placed in a Kjeldahl flask with 7 to 10 cc. of 15 per cent fuming sulfuric acid. (With easily decomposable substances, ordinary sulfuric acid is satisfactory.) The substance is dissolved, if possible, by gentle warming. Thirty per cent hydrogen peroxide (Superoxol) is added drop by drop, being allowed to flow down the side of the flask, which is agitated gently by hand. Oxidation takes place at once. Addition of hydrogen peroxide is continued until the liquid is the most straw colored, when warming is increased until fumes of SO_3 are abundant. Sometimes a little more hydrogen peroxide is required for complete decolorization; the total amount required will vary from 1 to 5 cc. It is essential that everything be in solution at this point. In the absence of halogen, no loss of

mercury was observed on heating, but in the presence of chlorine or bromine, too much warming is to be avoided. If desired, the reaction may be carried out under a reflux condenser as described subsequently. The reaction is complete when no more oxygen is evolved.

The water-white solution is diluted with water and precipitated directly with hydrogen sulfide, the mercuric sulfide filtered through a Gooch crucible, washed with carbon disulfide, alcohol, and ether, dried at 105° C. for 20 to 30 minutes, and weighed.

PROCEDURE IN PRESENCE OF IODINE. In the presence of iodine the decomposition must be carried out in a 200-cc. flask connected by a ground-glass joint to a spiral reflux condenser through which the hydrogen peroxide is added. During the oxidation as tested upon a mixture of mercurous and sodium tetraiodophenolphthalein, some iodine and mercuric iodide sublimes, and the solution is colored by dissolved iodine. The portion in the condenser is washed back several times with small amounts of water, and a little more hydrogen peroxide added to insure complete oxidation. A small final sublimate of iodine does no harm if it does not contain yellow mercuric iodide.

To the diluted liquid in the flask is added about 0.1 to 0.2 gram of aluminum powder (c. p.); on warming, a vigorous reaction takes place and a black sediment of amalgam settles out. Warming is continued (a little more aluminum may be added) gently for 15 to 30 minutes until the precipitation of mercury is complete and a small residue of aluminum metal remains unchanged. After cooling, this is filtered (suction) through a small folded filter which is returned to the flask in which the reduction has taken place. Under the reflux, 2 cc. of concentrated nitric acid and 3 to 5 cc. of bromine water are added. When the main reaction is over, a small drop of liquid bromine may be employed to dissolve the residual globules of mercury, which sometimes resist even prolonged warming without the bromine water.

TABLE I. ANALYSIS OF MERCURIALS BY VARIOUS METHODS

	CALCD. (KNOWN) %	JAMIESON TITR. %	JAMIESON GRAY. %	H ₂ S, AV. %
Metaphen	57.07	57.2		57.42
Merthiolate	49.55	49.44		49.05
Mercurochrome	24.93	24.84		24.88
Mercury salicylate	58.5 ^a	58.81 (KCNS)	59.1	58.25
Mercurosal	43-43.8 ^a		43.3	43.95
Mercuriofen	(51.5) ^a		51.71	52.14
Mercuric diphenyl	56.57		56.3	56.94
Mercurosal + tetraiodo- phenolphthalein	43-43.8			43.17

^a With those substances not completely pure, the average metal content as determined by several laboratories was selected.

The diluted contents of the flask are warmed to remove most of the bromine, filtered, and carefully decolorized with dilute sodium acid sulfate. Hydrogen sulfide is then passed in and the mercuric sulfide determined as described above.

The methods outlined have been tested upon standard samples of the six pharmaceutical mercurials listed below, upon pure mercury diphenyl, and upon more than a dozen synthetic mercury compounds to be described in a separate paper. The results of duplicate or triplicate determinations were in each case close either to theory, or to the known mercury content.

During the past three months, the method described above has been applied by the cooperating laboratories to the standard samples of the mercurials with "distinctly encouraging" results.

In the analysis of mercury ointments, the peroxide-sulfuric acid decomposition has been found more satisfactory than the official U. S. P. method employing nitric acid. In this analytical laboratory, it is now routinely applied to pharmaceutical preparations involving organic mercurials such as "Tincture Metaphen" and "Metaphen 2500." These

are merely concentrated rapidly to a small volume and the above procedure applied as usual.

ARSENIC

The decomposition of organic arsenicals is carried out in a similar manner. Because of the ease with which arsenic is determined volumetrically, volumetric methods have been employed almost exclusively, and that of Newberry (8) has been best adapted to the conditions at hand.

The solution after cooling is diluted with 100 to 150 cc. of water, and 10 cc. of 10 per cent potassium iodide are added. The liberated iodine is expelled by boiling and the liquid concentrated to about 40 to 50 cc. Any iodine is decolorized by one drop of sodium sulfite, the solution is made just alkaline with 20 per cent sodium hydroxide, then slightly acid with dilute sulfuric acid, and finally alkaline with 5 to 10 grams of sodium bicarbonate. It is then titrated with 0.1 *N* iodine, employing starch indicator at the end. The Lehman method (U. S. P.) may also be used. The results are given in Table II.

TABLE II

	KNOWN ARSENIC %	FOUND, AV. %
Arsphenamine	31.2	31.0
Neoarsphenamine	20.3	20.5
Sulfarsphenamine	21.6	21.4
Stovarsol	27.6	27.5

BISMUTH AND ANTIMONY

After decomposition as above, employing an excess of hydrogen peroxide, the bismuth and antimony exist as -ic sulfates. With hydrogen sulfide, precipitation was complete within 15 minutes, and no difficulty was encountered in filtration upon a Gooch crucible. The sulfides were precipitated in the presence of carbon disulfide, washed with this solvent, then with alcohol and ether, and dried at 100° C. for 30 minutes, or to the lowest weight observed. Although this procedure was satisfactory in the case of antimony, it was found better to reduce the dilute bismuth solution with sulfur dioxide solution, expel the excess of the latter by boiling, and precipitate as bismuth sulfide.

As alternative methods, precipitation of bismuth as basic carbonate and as metal (formaldehyde in alkaline solution) were tried with only moderate success. The results are given in Table III.

TABLE III

	KNOWN METAL CONTENT %	FOUND %
Potassium antimony tartrate + sugar	36.4	36.7
Bismuth subsalicylate	54+	54.5
Bismuth camphor carboxylate	40.5	40.7
Potassium bismuth tartrate + sugar	64.95	64.8

SILVER

The Superoxol decomposition was employed on several samples of silver protein in place of the more tedious nitric acid method. The diluted solution was titrated directly with potassium sulfocyanate after the addition of nitric acid and ferric sulfate. The results are given in Table IV.

TABLE IV

	KNOWN Ag %	FOUND %
Silver protein A	19.9	19.75
Silver protein B	19.9	19.93

GOLD

With gold, the reaction is different, hydrogen peroxide precipitating metallic gold.¹ It is therefore preferable to dis-

¹ N. A. Hansen of this organization has developed a similar method employing nitric acid.

solve soluble gold salts in dilute sulfuric acid, add 3 to 5 cc. of hydrogen peroxide, and warm. The precipitated mass of gold is washed with water, then with alcohol, dried at 105°C., and finally ignited. The results are as follows:

	CALCD. Au %	FOUND %
Gold sodium thiosulfate	37.0	37.0

GERMANIUM

The germanium compound is oxidized by sulfuric acid and hydrogen peroxide in a Kjeldahl flask, the sulfide precipitated from strongly acid solution, filtered as soon as coagulation is complete, and dissolved in strong ammonium hydroxide. This ammonia solution is filtered directly into a large crucible, the sulfide decomposed by Superoxol, evaporated to dryness, and ignited to germanium dioxide as in the method of Johnson and Dennis (4). The results are as follows:

	CALCD. %	FOUND %
Tetrabenzyl germanium	16.62	16.45

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Microdetermination of Carbon

Improvements in Nicloux Method

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THE method for microdetermination of carbon developed by Nicloux (3) would appear to have many possibilities, particularly in the field of biochemistry, since it is a comparatively rapid and moderately accurate method which can be applied both to organic compounds and to mixtures containing carbonaceous compounds either in the solid state or in solution. In its original form, the Nicloux method had many shortcomings, part of which were chemical and part technical. Boivin (1) has so modified the method as to overcome most of the difficulties which arose from faulty combustion and absorption of the resulting carbon dioxide. Various other modifications have been developed, as by Osuka (4), and Schadendorff and Zacherl (5), both of whom have improved the method of handling carbon-containing solutions, such as urine, etc. From the technical standpoint, the method remained clumsy and difficult to carry out. In this paper, further modifications are reported, aiming at the reduction of these technical difficulties and the simplification of the procedure. These modifications also make possible an increase in the accuracy and decrease the time necessary to carry out an analysis.

APPARATUS USED

The apparatus is shown in Figure 1. It is essentially the apparatus used by Boivin, except that instead of having a bulb blown directly in the upper chamber to hold the absorbing caustic solution, a detachable absorption chamber is introduced. The rubber tube at *G* in the Nicloux and Boivin apparatus is replaced by a stopcock, as well as the plunger type of stopcock in funnel *D*. Originally Nicloux used an ordinary stopcock in funnel *D* and later replaced it with the plunger type to prevent entrance of carbon from the stopcock grease. Such a replacement may be desirable but does not seem to be necessary from the authors' experience. In addition to the changes in design, it has been found advantageous to use the microfilters to be obtained from the Central Scientific Co., Chicago, Ill., previously described by Kirk and Schmidt (2) for separating the barium

carbonate precipitate, instead of centrifuging as in the original method.

PROCEDURE

A sample of dry material containing 2 mg. of carbon is weighed. Unless the percentage content of carbon is very low, this must be carried out on a microbalance, or by dilution of a weighed quantity of the unknown material with a larger weighed quantity of noncarbonaceous solid material and subsequent weighing of a sample of the mixture on an analytical balance. Dry sodium sulfate may serve for such a diluting material if allowance is made for it in adding the reagent later. The dry material is transferred to sample tube *A*. To this is added 0.6 gram of silver chromate and 0.1 gram of anhydrous sodium sulfate. The sample tube is attached to the upper part of the apparatus and 3 ml. of concentrated carbon-free sulfuric acid placed in funnel *D*. The sulfuric acid is rendered free from carbon by heating it under a good vacuum on a boiling water bath with a little chromate. This heating should take place behind a protective glass screen because of a certain risk from explosions. In one case out of a considerable number of such heatings, the reagent exploded with considerable violence. No reference to this hazard has been found in the literature.

If a stopcock is used, as shown here, it should be greased scantily with vaseline. The sulfuric acid apparently does not dissolve or attack the trace of vaseline with which it comes in contact. Another alternative is to use a phosphoric acid mixture as a lubricant, as described by Stevens (6).

The absorption cup, *C*, which is made from the bottom of a test tube, is now charged with 0.6 ml. of 2 *N* sodium hydroxide which must be carbonate-free. This is insured by the previous addition of a little barium hydroxide to the sodium hydroxide solution. The cup, inserted in the stopper containing a hole bored partly through, is inserted into chamber *B*. The system is now thoroughly evacuated and closed. In case any leakage develops, a little clear lacquer has been found to be very effective in sealing it without introduc-

ing difficulties. This, of course, must never come in contact with the oxidizing reagent, but may be safely applied around the stopper holding the absorption cup. Another possible point of leakage is the stopper through which filament *F* is introduced. De Khotinsky cement will seal this point and is practical for use, since this stopper need never be removed. It is likewise possible, if desired, to seal platinum or tungsten leads directly through the glass, rather than to use a stopper. Such seals are subject to considerable breakage due to heat from the filament.

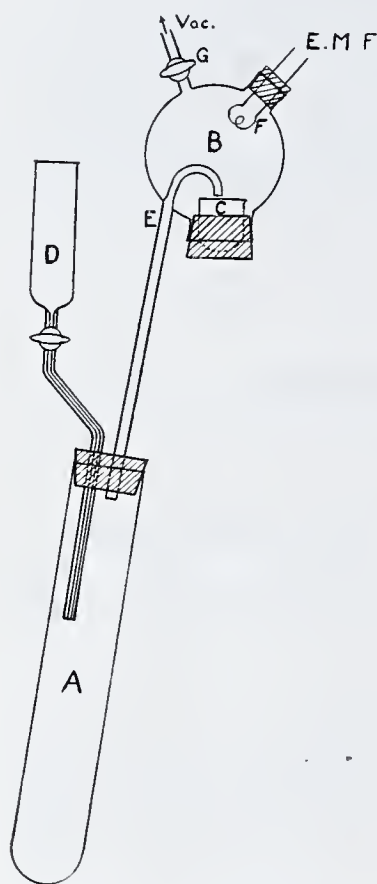


FIGURE 1. DIAGRAM OF APPARATUS

After evacuation, 2 ml. of the carbon-free sulfuric acid are run into *A* from the funnel. The tube is immersed in a boiling water bath for about 20 minutes. A microburner is then applied directly to the tube until the contents turn definitely green, which marks the end of the reaction. The tube is now cooled in a beaker of water and dilute sulfuric acid run in from the funnel until the liquid level is about 0.5 cm. from the end of tube *E*. A current of short duration is now passed through filament *F* by means of a tapping key. The current should be adjusted so as to heat the filament rapidly to a bright red color. A considerable number, fifty or sixty, of these intermittent currents are applied. The consequent heating and cooling of the filament catalyzes the oxidation of the carbon monoxide present to carbon

dioxide, and thoroughly circulates the gases over the caustic in cup *C*, producing complete absorption of carbon dioxide.

The procedure thus far has been that recommended by Boivin with the exception of the use of a different absorption apparatus. From this point on, it is decidedly preferable to abandon his method. The removable cup is simply taken out without disturbing the remainder of the apparatus, and the carbonate is precipitated in the cup with a solution of barium chloride. This is stirred thoroughly and immediately poured into a filter previously prepared as described by Kirk and Schmidt (2). The solution is sucked through and the precipitate thoroughly washed with water saturated with barium carbonate. Otherwise, either alkali is retained by the asbestos, or carbonate is dissolved. The precipitate is transferred to a test tube by pushing out the asbestos pad from the bottom of the filter with a small stirring rod. The cup and the sides of the filter are rinsed down by means of 0.05 *N* hydrochloric acid solution delivered from a microburet or accurate pipet, and followed by a little water. About 10 ml. of the acid are necessary to insure complete solution of the barium carbonate. A drop of methyl red is now added to the solution in the test tube, and the tube is heated by immersion in a boiling water bath until gas evolution ceases. The excess acid is back-titrated while still hot, using 0.05 *N* sodium hydroxide, and the methyl red as indicator. The acid required to react with the carbonate is

found by subtracting the base added from the total acid added, and the number of milligrams of carbon in the sample is obtained by multiplying the milliliters of 0.05 *N* acid by 0.3, since one ml. of 0.05 *N* acid is equivalent to 0.3 mg. of carbon.

A blank must be run on the reagents and, if the sulfuric acid is first heated with silver chromate as recommended by Boivin, this blank should not exceed 0.3 ml. of 0.05 *N* hydrochloric acid. The blank must be subtracted from the amount of acid used in the determination.

For analysis of physiological fluids, this method has been recommended by Boivin (1), Osuka (4), and Schadendorff and Zacherl (5). Urine analysis in particular is difficult on account of its content of volatile carbon compounds which are released in the evacuated chamber without undergoing oxidation. The method of Boivin for urine analysis has been tried and found to give unsatisfactory results. The last work mentioned undoubtedly avoids many of the difficulties of the Boivin technic. The modifications proposed here are equally applicable to any of these methods and will result in an improvement in the method.

RESULTS

Since the general method used is the same as that of Boivin it remains only to show that the modified method gives reliable results and is an actual improvement over the older type of technic. In Table I are listed a series of typical analyses of pure compounds.

TABLE I. TYPICAL ANALYSES OF PURE COMPOUNDS

SUBSTANCE	WT. OF SAMPLE	0.0502 <i>N</i> HCl	THEORETICAL C	AMT. OF C OBTAINED
	Mg.	Ml.	Mg.	Mg.
Sucrose	8.45	11.798	3.56	3.539
	7.67	10.743	3.23	3.22
	5.10	7.115	2.14	2.134
<i>p</i> -Amino-benzoic acid	3.20	6.61	1.98	1.983
	3.48	7.02	2.13	2.106
Tyrosine	3.58	6.996	2.135	2.098
	3.36	6.994	2.06	2.097
Glutamic acid	5.31	7.264	2.17	2.179
	5.13	7.10	2.09	2.13

From the results given in Table I it is seen that the method as modified compares very favorably with that of Boivin as regards accuracy when applied to pure compounds. In fact, it is theoretically possible to attain a higher degree of accuracy, since the exposure to the carbon dioxide of the air is reduced, the complete removal of the carbonate from the apparatus is more readily accomplished, and the filtration and washing give more nearly quantitative manipulation of the precipitate than is possible when the centrifuge method is used. In addition to the question of accuracy, the saving of time is considerable, which is particularly important in handling the absorption liquid to keep it free from carbon dioxide of the air. The ease of manipulation is considerably increased, thus making it possible to develop the necessary technic with a minimum of effort.

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Graphical Representation of Mineral Components in Water Analyses

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A GRAPHICAL method for expressing water analyses should depict adequately composition and significant relationships. Previously reported diagrams for representing results of water analyses include those of Tickell (4), Reistle (3), Collins (1), and others.

The method presented herein consists in plotting milliequivalent concentrations of the various ions along the sides of a rectangle in such a manner that its segmentation, form, and size completely describe the dissolved minerals. Referring to Figure 1, the construction of the rectangular diagram from an ionic analytical statement is as follows:

Let OX and OY be horizontal and vertical coordinate axes, respectively. On OY scale off a length, Oa , proportional to the magnitude of chloride ion in the water. Starting at a , lay off a length, ab , proportional to the amount of sulfate. At point b , perpendicular to axis OY lay off bc proportional to the bicarbonate content, or in cases where both bicarbonate and carbonate ions are present together, the equivalent of their sum may be used. Drop from point c a perpendicular, cd , to axis OX . To represent cations, commence at point b and lay off be proportional to calcium and ec plus cf proportional to magnesium. If in a sample calcium is greater than bicarbonate, then point e will be located on vertical dc . The residual length, fd , represents the amount of sodium present and may be used in this way to solve graphically for the sodium content of a water or to check the analytical value obtained therefor. In most cases the alkali ions sodium and potassium may be considered entirely as sodium. The lengths be , representing calcium, and ec , a part of the magnesium, might just as well have been located along the base od , except that this part of the diagram as drawn gives the advantage of coincidence to aid in comparisons.

RELATIONSHIPS

A rectangular diagram can readily be drawn on ordinary graph paper and shows at a glance several important characteristics of the water. The perimeter represents the total concentration of minerals in the water; one-half of the perimeter measures the normality of the solution. Relative lengths of segments indicate relative concentrations of the various ions.

The width of the figure shows the so-called temporary hardness, or more properly the carbonate hardness of the water. Segments be and $(ec \text{ plus } cf)$ indicate relative amounts of calcium and magnesium; their sum represents the total hardness. Incrustants, or noncarbonate hardness, is shown by the length cf . If a water sample shows negative hardness, point f will lie somewhere along the line bc , in which case segment fc will geometrically represent the amount of negative hardness.

The sulfate-carbonate ratio, if the water is completely softened by zeolites for boiler feed, is indicated by the ratio of segments ab to bc , or the slope of the diagonal ac .

As it stands, the diagram pairs off cations and anions by assigning them homologous positions. No imaginary compounds are hypothecated. All graphical relationships arise solely from the choice of appropriate positions for the various ions.

For waters constitutionally similar but varying no matter

how widely in total concentration, rectangular diagrams are geometrically similar. Only the size will change.

If a water undergoes change chemically, its diagram will vary in size, shape, or in special cases, merely by segmentation.

Although the width of the diagram for a typical natural water may become relatively small by elimination of bicarbonate through treatment to its solubility limit, the figure will in general retain its height except in cases where sulfate is changed intentionally by addition of some soluble sulfate, or is reduced by barium softening.

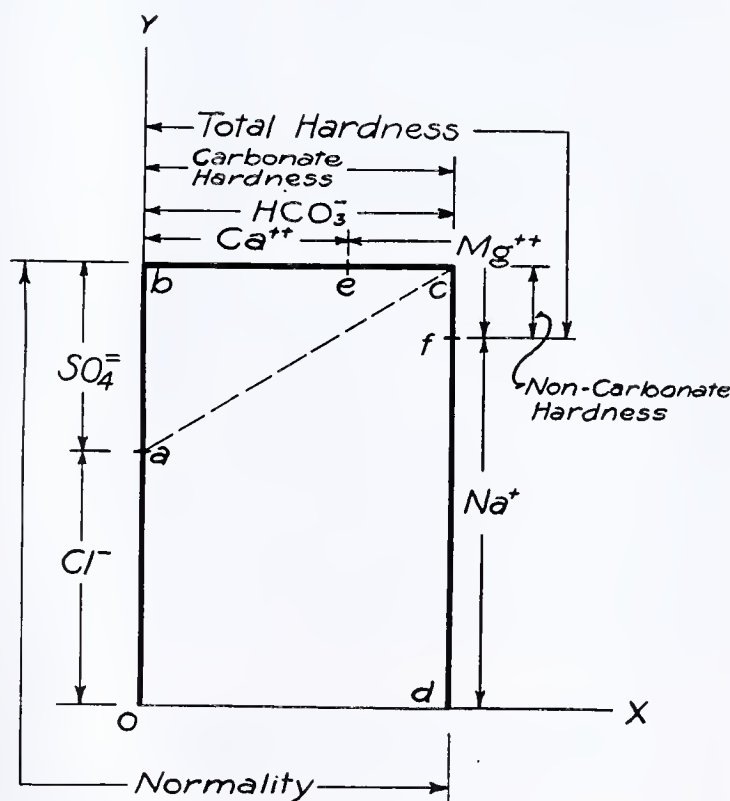


FIGURE 1. CONSTRUCTION AND SOME PROPERTIES OF RECTANGULAR DIAGRAM

In special instances of waters having unusual composition, such as those from some mineral springs, any rarely occurring ions may be included in the diagram in positions occupied by chemically similar ions. For highly siliceous water, the silicate radical should be included in the figure.

In segment bc the carbonates have been reduced to equivalent bicarbonate ion mainly because the bicarbonate condition is usually associated with natural waters. If preferred, this detail may be reversed and the carbonate ion plotted instead. If maximum differentiation is desired, the proportion of carbonate and bicarbonate may be indicated by a secondary division along line bc . Free carbon dioxide may be appended in the diagram by extending line bc across its intersection with the vertical dc . Since the ratio of free carbon dioxide to the bicarbonate alkalinity in many waters is an index of the pH, as shown by Greenfield and Baker (2), the diagram affords a graphic approximation thereof. When representing acid mine or volcanic waters, the total amount of titratable hydrogen ion should be plotted as a cation, preferably

along the upper base, *bc*. Similarly to represent the causticity of boiler waters, the hydroxyl ion should be plotted as a segment along *bc*.

APPLICATIONS

As an illustration of the utility of the rectangular diagram, a specific application of this method to represent the municipal water supply of New Orleans both before and after purification by the lime-iron process is given in Figure 2. Average

analyses sodium is obtained by calculation, the difference between the values reported for this ion in river and in filtered waters arises from cumulative errors in sampling, storage, and analysis. It should be noted that free carbon dioxide in river water and residual bicarbonate alkalinity in treated water are plainly indicated in the plot.

TABLE I. AVERAGE ANALYSES OF MISSISSIPPI RIVER WATER AND OF NEW ORLEANS TAP WATER FOR 1931

ITEM	EQUIV. WT.	1			
		RIVER WATER	TAP WATER		
		P. p. m.	Milli-equiv./liter	P. p. m.	Milli-equiv./liter
SiO ₂	5.9	...	7.8	...
Fe ₂ O ₃ }	0.0	...	0.0	...
Al ₂ O ₃ }					
CATIONS:					
Ca	0.0499	38.6	1.926	16.8	0.839
Mg	0.0822	10.0	0.822	7.1	0.584
Na	0.0435	18.5	0.806	22.8	0.992
ANIONS:					
HCO ₃	0.0164	115.9	1.900	45.0	0.738
SO ₄	0.0208	41.9	0.872	43.0	0.895
Cl	0.0282	27.7	0.782	27.7	0.782
Solids by analysis (all HCO ₃ as CO ₂)					
		201.5		148.1	
Solids by evaporation					
		221		158	
Incrustants (as CaCO ₃)					
		29.4		33.3	
Alkalinity (as CaCO ₃):					
Methyl orange		95.0		36.9	
Phenolphthalein		0.0		16.4	
Free CO ₂		1		0.0	

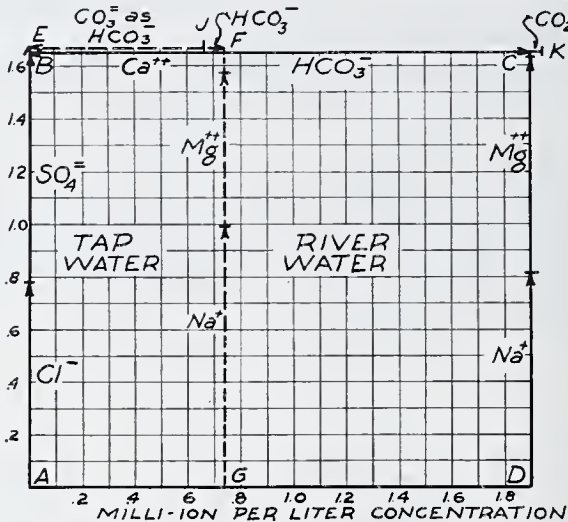


FIGURE 2. RECTANGULAR DIAGRAMS FOR NEW ORLEANS WATER SUPPLY

analyses for the past year are given in Table I. The solid lines, rectangle *ABCD*, represent the mineral analysis of raw Mississippi River water. This plot shows clearly that river water is relatively low in dissolved solids, fairly hard, most of the hardness is due to calcium, magnesium is small relative to calcium, and the molar sulfate carbonate ratio is about 0.5. The smaller rectangle, *AEFG*, represents the composition of partially softened tap water and indicates reduction principally in calcium and bicarbonate. Magnesium has been reduced slightly, but noncarbonate hardness just barely increased by addition of the coagulant. The molar sulfate-carbonate ratio has been doubled. Since in the

If all hardness were removed by zeolite treatment, the rectangle *AEFG* would still show the anions in the completely softened effluent, but the sides *EF* and *FG* would now represent sodium.

A single set of related rectangles has thus effectively described the characteristics of a given water and its modifications.

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Determination of Benzene in Solvent Mixtures

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A SIMPLE and rapid method for the detection and estimation of benzene in solvent mixtures, of sufficient sensitivity to be further adapted to the determination of the concentration of benzene vapors in air when of interest from a health standpoint, has been deemed necessary. This method should make the results attainable immediately in the plant without reverting to the laboratory. There are data available (?) to show that concentrations of benzene in air as low as 100 parts per million are objectionable. Since the type of absorption apparatus usually employed for collecting samples of vapors in air handles a liter of air per minute, a 30-minute run would make only about 0.012 ml. of benzene available when the above concentration occurs. Consequently, it was considered necessary to have a method of sufficient sensitivity to detect this small amount. This discussion will be confined to a survey of possible

methods, their relative advantages and disadvantages, and a description of sufficient experimental data covering two methods investigated in the laboratory, one of which fulfils the above requirements rather well and is adaptable where there is as little as 0.010 ml. of benzene available in the liquid phase. In a subsequent work the authors hope to show that this method is also adaptable to the determination of benzene in air.

POSSIBLE METHODS

Four reactions were found in the survey of the literature which gave promise of being applicable.

1. Bromination in presence of anhydrous aluminum bromide (4).
2. Nitration with a mixture of concentrated sulfuric and fuming nitric acids (5).

3. The "pernitric acid" method (6).
4. The oxidation method with hydrogen peroxide in presence of iron salts (2).

BROMINATION. The method of Gustavson (3) for the detection of aromatic hydrocarbons in gasoline is based on complete bromination in the presence of anhydrous aluminum bromide. The hexabromobenzene and the pentabromotoluene are crystalline products, whereas the aliphatic bromine compounds are liquids. Because of this, the hexabromobenzene and pentabromotoluene may be filtered off and weighed. Schultz (4) has shown that even a few milligrams of benzene

of lower (aqueous) layer with a pipet. To these 3 ml. add a piece of sodium hydroxide about the size of a small pea. Formation of a distinct brick-red ring at bottom of the test tube indicates presence of benzene.

This method, as well as slight improvements on it, such as use of nitric acid and hydrogen peroxide in place of sodium nitrite, hydrogen peroxide and sulfuric acid mixture and also alcoholic potassium hydroxide in place of solid sodium hydroxide, were tried. The limit of sensitivity was 0.05 ml. of benzene, and in this range one ml. of toluene produced approximately the same color reaction.

This method is regarded as unsatisfactory because the preparation of nitric oxide or its transportation in sufficient amount in the field is relatively inconvenient, and because toluene seriously interferes at the lower limits of sensitivity on the reaction.

OXIDATION METHOD BY MEANS OF IRON SALTS AND HYDROGEN PEROXIDE

Since the authors were not interested in the reaction of large quantities of benzene but rather in the development of the reaction to give a test for the smallest possible amount of benzene, experiments were first run to arrive at the optimum amounts and concentrations of the reagents for this purpose. It was found that a reddish brown coloration developed and a fine black precipitate was formed on the addition of 5 ml. of 0.5 per cent ferrous sulfate solution and 2 ml. of one per cent hydrogen peroxide to as little as 0.01 ml. of benzene. Even amounts down to 0.005 ml. of benzene caused the development of the characteristic

reddish brown coloration. In conducting these tests, the benzene was measured in a capillary pipet of such bore that the hundredth milliliter graduations were a centimeter apart. On account of its convenience, the volumetric measurements were used and considered permissible since careful technic was observed and gravimetric checks run from time to time.

A group of experiments was then conducted to determine whether other solvents interfered with this reaction. It was found that most other solvents inhibited the reaction, and that generally the more water-soluble, the smaller the amount necessary to cause interference.

DESCRIPTION OF APPARATUS. In order to avoid this interference, an apparatus was designed to remove the more water-soluble substances from the solvent mixture. This is illustrated in Figure 1. It consists of a vaporizing tube, A, a bubbler type absorption bottle, B, and a trap, C, immersed in a freezing mixture of solid carbon dioxide in acetone. These units are joined by ground-glass connections. A rubber tube attached to the flowmeter leads to suction. The capillary part of the vaporization tube is graduated to 0.02 ml. and has a capacity of slightly more than 0.3 ml.

EXPERIMENTAL PROCEDURE. One- to three-tenths milliliter of the solvent mixture is placed in the vaporizing tube, and air drawn through the apparatus at the rate of one-third liter per minute. To facilitate vaporization, a capillary is inserted well into the vaporizing tube. The vapors are bubbled through the absorption bottle in which are placed 25 ml. of water. A small amount of pure benzene is run through the apparatus previously in order to saturate the water under

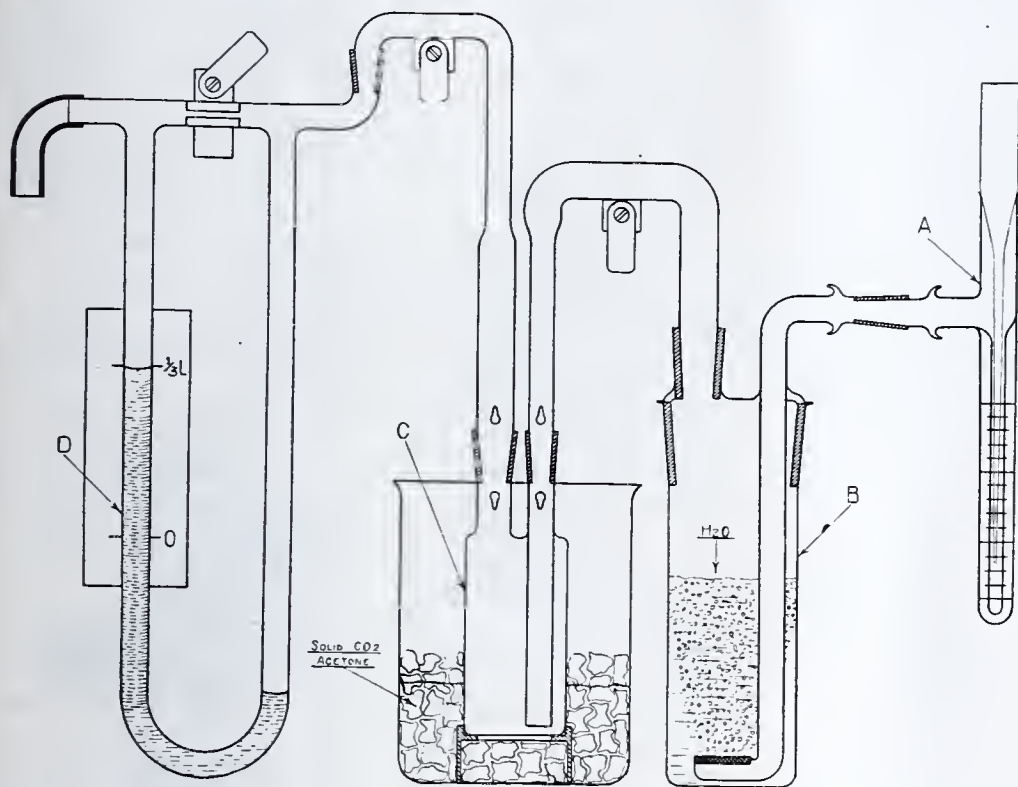


FIGURE 1

or toluene can be determined in air in the presence of ethylene. For the purpose desired, this method is regarded as unsatisfactory by the authors for the following reasons: The necessity of using bromine and aluminum powder was objectionable in field work; washing, drying, and weighing the precipitate are manipulations which are not feasible in field work; and the test for benzene is not specific.

NITRATION WITH CONCENTRATED SULFURIC AND FUMING NITRIC ACIDS. This method involves, after the absorption and nitration of the benzene by a mixture of concentrated sulfuric and fuming nitric acids, the steam distillation of the nitration product, *m*-dinitrobenzene. The *m*-dinitrobenzene is quantitatively reduced in an excess of standard titanous chloride, the excess of this reagent being estimated by ferric chloride using potassium thiocyanate as indicator. In the words of the investigator (5), "The method is admitted to be somewhat cumbersome and slow, but it is specific for benzene in the presence of many compounds known to be interferences in previously used methods. It will satisfactorily estimate benzene for hygienic purposes in the presence of as much as four times as much toluene as benzene, which is a strong point in its favor." In view of the foregoing, this method does not meet the authors' requirements.

PERNITRIC ACID METHOD. This method as used by Trufonow (6) is as follows: To 2 ml. of the sample add 4 ml. of an equivolume mixture of 4 per cent sodium nitrite solution and a 3 per cent hydrogen peroxide solution. Shake thoroughly. Add 2 ml. of 2 *N* sulfuric acid and again shake thoroughly. Allow to stand for one minute and remove 3 ml.

these conditions. Most of the benzene and a small portion of the more water-immiscible solvents pass over into the trap which is placed in an acetone-solid carbon dioxide bath. Here the benzene is frozen out of the air stream and deposited. After passing air through the system for 2 minutes, the trap is removed. Five milliliters of 0.5 per cent ferrous sulfate are directed down the inlet tube, followed immediately with 2 ml. of one per cent hydrogen peroxide. Both these reagents should be made up shortly before running the tests. The trap is shaken 2 minutes and the contents poured into a test tube. If benzene is present in amounts of 0.010 to 0.050 ml. in the solvent mixture added to the vaporizing tube, a brown coloration suddenly develops and then an amorphous black precipitate. This may occur in 2 to 5 minutes after the crystals in the trap have melted.

A procedure which assisted in the utilization of this method quantitatively was developed as follows: 0.200 ml. of the solvent mixture is placed in the vaporizing tube, the procedure outlined above is followed, and the results noted after the reaction mixture has been removed from the trap and allowed to stand for 3 minutes. If the black amorphous precipitate is formed, 0.010 ml. or more benzene was present. (Between 0.010 and 0.012 ml., the black precipitate is produced in an exceedingly finely divided state and does not coalesce or readily settle out. Therefore, it is desirable for the one conducting the test to run through the procedure and determine exactly the minimum amount of benzene which, in his opinion, gives the black precipitate.) The total amount of solvent placed in the vaporizing tube should then be decreased until the reaction mixture just shows the black amorphous precipitate. Since 0.010 ml. is the minimum amount of benzene which will produce this precipitation, the percentage of benzene in the solvent mixture can be calculated.

If the characteristic brown coloration develops without the black precipitate, 0.005 ml. or more benzene was present. Both in this case and also when there is no reaction, an indication of the presence of benzene, qualitatively and quantitatively, may be obtained by running a series of tests in which measured amounts of pure benzene are added to the solvent mixture.

Upon the addition of 1 ml. of 2 *N* nitric acid, the black amorphous precipitate will dissolve and the solution may then be diluted with water and compared with standards. This colorimetric method permits greater accuracy in the quantitative estimation of benzene.

If carbon disulfide is present, amorphous sulfur is liberated. This is of course not dissolved on the addition of the nitric acid and should be filtered from the solution. The benzene may then be estimated from the coloration of the filtrate.

Inasmuch as this reaction is decidedly complicated, yielding a mixture of phenol, catechol, hydroquinone, and the black amorphous precipitate mentioned above, it could hardly be expected that the colors of the resultant liquid described in the preceding paragraph would lend themselves to anything more than a rough quantitative estimation, except over a very narrow range such as around 0.010 ml., as described above. For the same reason it is highly important to observe the same technic in all tests. However, the entire estimation takes less than 10 minutes to run, so the number of these estimations can be run rather economically in order to get the desired quantitative accuracy.

Table I shows the results obtained with the reaction on mixtures of benzene and various other solvents. The solvents listed include most of those ordinarily used for industrial operations and having boiling points relatively near that of benzene. Solvents boiling at temperatures appreciably higher than the boiling point of benzene were not included, since they would not be sufficiently vaporized under the experimental conditions to impede the reaction.

TABLE I. EXPERIMENTAL RESULTS

AMT. OF BENZENE ML./1000	OTHER SOLVENTS	AMT. TAKEN ML./1000	REACTION
0	Toluene	200	None
10	Toluene	90	Black ppt.
20	Toluene	200	Black ppt.
0	Xylene	200	None
10	Xylene	90	Black ppt.
20	Xylene	200	Black ppt.
0	Methanol	200	None
10	Methanol	90	Black ppt.
20	Methanol	200	Black ppt.
0	Ethyl alcohol	200	None
10	Ethyl alcohol	90	Black ppt.
20	Ethyl alcohol	200	Black ppt.
0	Isopropanol	200	None
10	Isopropanol	90	Black ppt.
20	Isopropanol	200	Black ppt.
0	<i>n</i> -Butanol	200	None
10	<i>n</i> -Butanol	90	Black ppt.
20	<i>n</i> -Butanol	200	Black ppt.
0	Isobutanol	200	None
10	Isobutanol	90	Black ppt.
20	Isobutanol	200	Black ppt.
0	<i>n</i> -Amyl alcohol	200	None
10	<i>n</i> -Amyl alcohol	90	Black ppt.
20	<i>n</i> -Amyl alcohol	200	Black ppt. cleared to brown
0	Ethyl acetate	200	None
10	Ethyl acetate	90	Black ppt.
20	Ethyl acetate	200	Brown
0	Ethyl propionate	200	None
10	Ethyl propionate	90	Black ppt.
0	<i>n</i> -Butyl acetate	100	None
10	<i>n</i> -Butyl acetate	90	Black ppt. cleared to brown
0	Isoamyl acetate	200	None
10	Isoamyl acetate	90	Black ppt.
20	Isoamyl acetate	200	Black ppt.
0	Ethylene chloride	100	None
20	Ethylene chloride	20	Black ppt.
0	Trichloroethylene	100	None
20	Trichloroethylene	20	Brown ppt.
0	Tetrachloroethane	200	None
20	Tetrachloroethane	200	Black ppt.
0	Carbon tetrachloride	100	None
10	Carbon tetrachloride	90	Black ppt.
0	Acetone	200	None
20	Acetone	200	Black ppt.
0	Carbon disulfide	100	Soln. greenish, amorphous sulfur ppt.
10	Carbon disulfide	90	Black ppt. plus amorphous sulfur
0	Cellosolve	200	None
10	Cellosolve	100	Black ppt. cleared to brown
20	Cellosolve	200	Black ppt. cleared to brown
0	Gasoline	200	None
20	Gasoline	200	Black ppt.
MIXTURES			
0	Equivolume mixture of all solvents above, except carbon disulfide	200	None
20	Equivolume mixture of all solvents above, except carbon disulfide	200	Brown ppt.
0	Equivolume mixture of toluene and xylene	200	None
20	Equivolume mixture of toluene and xylene	200	Black ppt.
0	Equivolume mixture of 6 alcohols above	200	None
20	Equivolume mixture of 6 alcohols above	100	Black ppt.
0	Equivolume mixture of 3 acetates above	200	None
20	Equivolume mixture of 3 acetates above	200	Black ppt.

ACKNOWLEDGMENT

The authors wish to express their appreciation to Eimer and Amend, New York, N. Y., for the helpful suggestions in designing the apparatus shown in Figure 1.

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RECEIVED June 10, 1932.

New Aliquot and Filter Devices for Analytical Laboratories

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IN THESE laboratories large numbers of mechanical analyses of soils have to be made as a part of the service routine. It is desirable to make these as rapidly as is possible, consistent with accurate results. In this work there have been developed recently two devices which have materially speeded up the process and diminished errors due to the personal equation. These devices are of general utility wherever processes of similar type are employed in routine procedure, and may therefore be of general interest.

SUSPENSION ALIQUOT DEVICE WITH DEPTH CONTROL

In the course of a mechanical analysis by the pipet method (1), three aliquots are taken using a Lowy pipet, which is lowered into the suspension to the proper depth. In ordinary routine, suspensions of eight soil samples are placed in sedimentation cylinders for pipetting. The samples are pipetted with a regular time interval between them. This means the depth at which the aliquot is taken is the same for the set of eight samples. It was with this idea in mind and in an effort to eliminate errors in lowering the pipet to the correct depth that the following device was developed. It makes possible the lowering of the pipet definitely to any prearranged depth and repeating the operation any number of times without a change in setting.

From Figure 1 it will be seen that the device consists of a frame, *A*, *B*, *C*, supporting two parallel rods, *D* and *E*, which serve as rails. Upon them three parallel blocks, *F*, *G*, *H*, slide. *G* is provided with clips, *J* and *K*, with which the pipet is secured firmly. *F* and *H* serve as limits, limiting the travel of *G*. *L*, *M*, and *N* are thumb wheels used in securing the position of *F*, *G*, and *H*. *O* is a calibrated rod used in adjusting the distance between *F* and *H*—i. e., depth of pipetting.

For smooth operation, a good mechanical construction is necessary. Blocks *F*, *G*, and *H* should have good bearing surfaces, and if rods *D* and *E* are in alignment, no jamming or chattering of *F*, *G*, or *H* should result. Any shaking of *G* would result in undue disturbance of the suspension.

In operating, the procedure is as follows: The pipet is inserted in clips *J* and *K* provided on *G*. *N* is loosened and the upper edge of *H* is set against the scale on *O* at the desired depth of pipetting. *N* is tightened and requires no further attention until a new depth is used. The pipet

tip is brought directly over the suspension. *M* is loosened and *G* allowed to descend until the tip of the pipet touches the top of the suspension. *F* has also descended with its lower face in contact with the upper face of *G* (Figure 2). *L* is tightened and *G* allowed to descend again until its lower surface is in contact with the upper surface of *H*. At this point the pipet has reached the desired depth and the aliquot is taken. When this has been done, *L* is released and *G* is raised as far as it will go, carrying with it *F* and its associated parts. When the pipet is clear of the suspension, *M* is secured and the pipet is removed from *J*, *K*. The time consumed in the complete operation, exclusive of filling the pipet, usually does not exceed 10 seconds.

Over a period of 15 months the device has proved to be accurate, rapid, trouble-free, and labor-saving. Its cardinal advantage lies in the feature whereby, once set for a particular depth, the accuracy of this most important factor is insured throughout the series of samples.

NEW FILTER RACK

In the analysis of a large number of samples by the pipet method (1), a considerable amount of filtering is necessary. The filtering is done by means of Pasteur-Chamberland filter tubes, using the laboratory vacuum, and the filtrates are saved for evaporation and determination of soluble material. To aid in this work, a filter rack was developed. Figure 3 shows this device as used in this laboratory, connected to the filters shown in the foreground. Figure 4 shows the

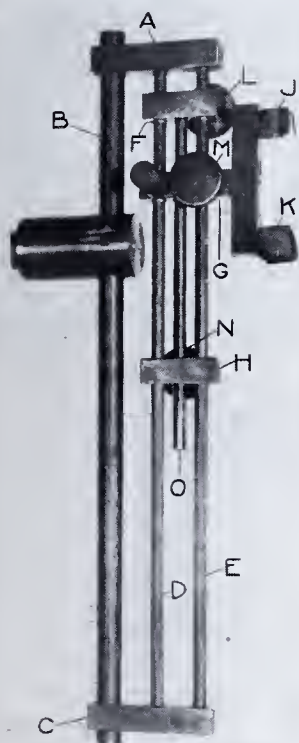


FIGURE 1. SUSPENSION ALIQUOT DEVICE

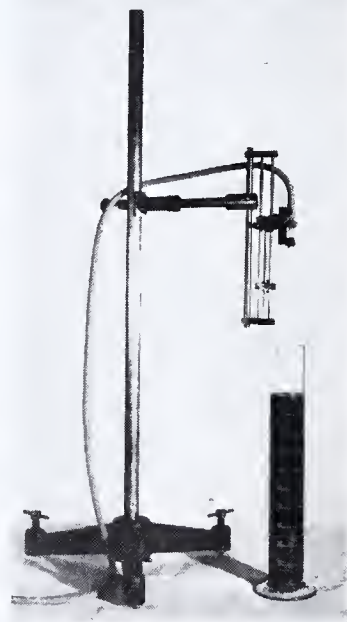


FIGURE 2. SUSPENSION ALIQUOT DEVICE IN PLACE



FIGURE 3. FILTER RACK

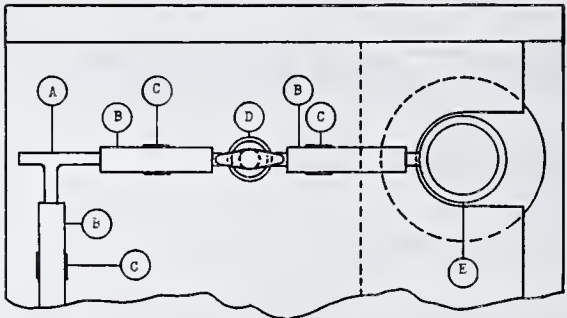


FIGURE 4. TOP VIEW OF UNIT OF RACK
A, glass T; B, rubber tubing; C, clamp; D, stopcock;
E, suction flask

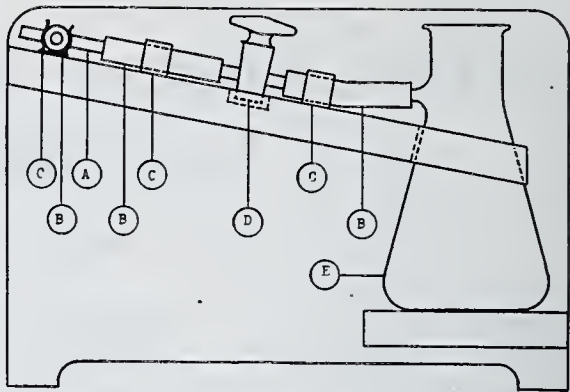


FIGURE 5. SIDE VIEW OF UNIT OF RACK
A, glass T; B, rubber tubing; C, clamp; D, stopcock;
E, suction flask

top view of one of the units, and Figure 5 is a side view of the same unit. As now constructed, the rack is composed of eight such units (Figure 6). The frame is constructed of ordinary 3/4-inch lumber finished with a heavy coat of shellac as protection against moisture. In Figure 5 the inclined shelf may be seen. Upon this shelf the manifold and stopcocks are mounted by means of brass clips. The shelf serves a double purpose in that it affords a means of securing the parts and helps to prevent possible contamination of the filtrates should they spray or foam up into the connecting tubes. Flasks of 250 ml. capacity are used, and since 200 to 700 ml. of filtrate are required, the flasks have to be emptied several times. This is accomplished easily, as the filters are disconnected from the flasks and removed in a group, leaving the flasks completely accessible from the front and in position to be disconnected with an ease comparable to that of breaking an electrical connection by means of the conventional attachment plug. After emptying, the flasks are replaced in the same manner. Since the rubber connections are securely fastened and in individual units, the analyst is spared the confusion attached to the usual tangle of loose



FIGURE 6. FILTER RACK OF EIGHT UNITS

tubing, glass T connections, and flasks. The individual stopcocks afford several conveniences: The rack may be used for less than the usual number of samples by simply turning off the unused units, or, if a few samples filter before the others of the group, they may be cut out and all of the vacuum utilized in speeding up the remaining ones. In addition to its present use, it is quite possible that the rack may be used in connection with other filtering devices such as Büchner

funnels, conventionally mounted in the mouths of the filter flasks. Uneven distribution of vacuum may easily be cleared up by inserting additional T's at convenient places in the manifold; one connection at each end is used at present. The number of units in the rack may be varied to suit the individual need of the user.

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RECEIVED June 27, 1932.

Selenium in Determination of Nitrogen by Kjeldahl Method

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LAURO (2), from results on cereal extracts, has suggested the use of selenium in place of copper sulfate as a catalyst to reduce the time of digestion in Kjeldahl nitrogen determinations. In the aqueous extracts used in the Allergy Clinic of the New York Hospital, standardization is based on the nitrogen content as determined by the conventional Kjeldahl method (1). As the digestion of these extracts required several hours, Lauro's modification was applied to their standardization. It will be evident from Table I that these extracts are of wide variety. Analyses of extracts, on which parallel nitrogen determinations were run using copper sulfate and amorphous precipitated selenium, showed checking results with a decrease of one-half to two-thirds the time necessary for digestion where selenium was used. Owing to the variation in burners and the fact that heating in some cases was carried on longer than necessary in order to assure complete digestion, the time factor is not absolute. The results were considered sufficiently conclusive to adopt the modification in these analyses.

TABLE I. ANALYSES OF EXTRACTS				
EXTRACT	COPPER SULFATE		SELENIUM	
	Mg. N/cc.	Min.	Mg. N/cc.	Min.
Date	0.53		0.55	
Pumpkin	0.17		0.53	
Potato flour	0.07	180	0.18	
	0.04		0.06	120
Horse epithelium	0.26	150	0.27	75
Green pepper	0.88	300	0.86	150
Guinea pig epithelium	1.26	165	1.26	90
Pumpnickel	0.58		0.56	
Birch pollen	0.43	140	0.42	50
Ash pollen	0.58	140	0.60	75
Oak pollen	0.92	175	0.94	135
Poplar pollen	1.00	170	1.00	85
Plantain pollen	0.43	215	0.45	135
Ragweed pollen 1	0.39	180	0.37	90
Ragweed pollen 2	0.98	170	0.99	95
Ragweed pollen 32	0.62	165	0.63	90
Timothy pollen 31	0.31	170	0.32	90
Timothy pollen 32	0.40	135	0.40	60
Cashew nut	3.73	180	3.72	150
Urine 1	7.29	75	7.26	35
Urine 2	9.85		9.90	

(1) Assoc. Official Agr. Chem., *Methods*, 2nd ed., 1925.
(2) Lauro, M. F., *IND. ENG. CHEM., Anal. Ed.*, 3, 401 (1931).

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Determination of Sulfuric Anhydride in Sulfonated Oils

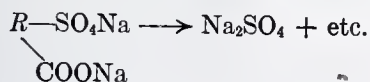
New Titration Method

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ONE of the most important determinations in the analysis of sulfonated oils is the amount of organically combined sulfuric anhydride. This may be in the form of a sulfate—that is, a sulfonic acid ester—or a true sulfonic acid. The former is characterized by the formula $R-O-SO_3H$ and the latter by $R-SO_3H$, where R represents the fatty radical. An essential difference between the two compounds is the fact that the sulfonic acid esters split off sulfuric acid when heated with mineral acids, whereas the true sulfonic acids are stable under such conditions.

The writer (3) in 1917 proposed a volumetric method, now widely used in practice, for the determination of organically combined sulfate in sulfonated oils of the ester type, which eliminated two barium sulfate determinations required in the old gravimetric method. It is based upon the principle that when the oil is boiled with mineral acids, one molecule of the neutralized sulfonated oil liberates one molecule of sodium acid sulfate, according to this formula: $R-O-SO_3Na + H_2O \longrightarrow ROH + NaHSO_4$. The method consists in heating the oil with a given quantity of standardized sulfuric acid and determining the increase in acidity after boiling. Some objections have been raised against the method because of the difficulty in observing the end point, since the titrations are made in the presence of oil. It has also been stated that the results are somewhat low when compared with the acid gravimetric method, owing to incomplete decomposition. Finally it is claimed that the method is inapplicable in the presence of sodium acetate since all the sodium is not completely titrable in presence of methyl orange, the indicator used.

A new titration method, hereafter called "ash-titration" method, is outlined below which is based upon the principle that when the completely neutralized sulfonated oil is ashed, the organically combined sulfate is quantitatively converted into sodium sulfate. The reaction is as follows:



It will be noticed that one mole of sodium hydroxide or its equivalent combined with the carboxyl group corresponds to one mole of sodium sulfate. Since the former can be accurately determined, it follows that the organically combined sulfate can readily be estimated. The method consists in ashing a mixture of the oil and excess standardized caustic, and finding the loss in titrable alkali after ignition. The loss in alkalinity—i. e., the difference between the alkali added plus the fixed alkalinity of the sample and the alkali found after ignition—is calculated to organically combined sulfate according to the following formula: one mole KOH \approx one

A new titration method is outlined, based upon the absorption of alkali when the sulfonated oil is ashed. It is more rapid than the old acid-boiling titration method, particularly where many analyses are to be run at the same time. The new method yields better check results and requires fewer reagents. The values for organic sulfur are higher, indicating either more complete decomposition or the presence of true sulfonic acids. The method, however, does not determine the organic sulfur in sulfonated mineral oils or other nonsaponifiable oils or salts. It is suggested that it may also be used as a qualitative test for sulfonation.

mole SO_3 . This relationship, instead of two moles of potassium hydroxide being equivalent to one mole of sulfate, holds true since the sulfuric acid in the oil is already half neutralized.

PROCEDURE

Two determinations are required: "fixed alkalinity," and "decrease in alkalinity after ashing."

FIXED ALKALINITY (A_F). This refers to the nonvolatile alkali and, in the absence of ammonia or other volatile alkali, it is determined as follows: Ten grams of the oil are dissolved

in 50 cc. of water in a 250-cc. Erlenmeyer flask, 50 cc. of 25 per cent neutral salt solution added, and the mixture titrated to an approximate end point in the presence of 5 drops of methyl orange (1 per cent solution, dissolved hot, cooled, and decanted). The contents are transferred to a separatory funnel, the flask rinsed with 3- to 15-cc. portions of ether, which are added to the separatory funnel, and the mixture made distinctly acid with standardized solution. After shaking and separating, the lower layer is drawn off into a 250-cc. beaker. The ether layer is washed with 15-cc. portions of the salt solution until the wash water is neutral to methyl orange, first rinsing the flask with them. The combined water layers are warmed to expel ether, two drops of methyl orange are added, and the titration completed, approaching the end point with acid. The result is calculated to milligrams of potassium hydroxide per gram of sample and denoted by A_F .

In the presence of ammonia, the fixed alkalinity is determined in the following manner: Five grams of the oil are dissolved in 100 cc. of water in a 400-cc. beaker, 25 cc. of 0.5 *N* sodium hydroxide are added, and the solution boiled until wet litmus paper no longer indicates ammonia. The rest of the procedure is according to the above. The fixed alkalinity in this case is given by the difference in the alkalinity after boiling and the amount of alkali added, and is readily calculated according to the following formula (acid and alkali used in titration, in milligrams of potassium hydroxide):

$$\text{Fixed alkalinity } (A_F), \text{ mg. KOH per gram} = \frac{\text{total acid} - \text{total alkali}}{\text{sample}}$$

In this connection it is to be observed that the change in the presence of methyl orange at the neutral point when titrating with acid is from a yellow color to a faint orange. The following method for noting this change accurately is suggested: Titrate to an approximate end point, leaving the solution slightly but distinctly on the alkaline side, and transfer about 30 cc. into a 100-cc. beaker (beaker 1). Continue with the titration in the original beaker, adding one or two drops of

the acid at a time, and transfer after each addition 30 cc. of the solution into another 100-cc. beaker (beaker 2). If upon comparing beakers 1 and 2 there is no change in color, contents of the latter are poured back into the original beaker and the titration continued until a change is just noted. Beaker 1 is now carefully titrated until it just matches beaker 2. Very slight change in the color of the solution is readily detected by this procedure, whereas over-titration is likely by the usual method.

DECREASE IN ALKALINITY AFTER ASHING. Five grams of the oil in a 30-cc. platinum or porcelain evaporating dish are mixed with an equal quantity of 1 *N* sodium hydroxide, using a small glass rod for stirring. The solution is evaporated to dryness either in an oven or over a free flame, the residue heated until it catches fire, allowed to burn gently, and the ash ignited for about 10 minutes, or until the carbon is nearly consumed. The stirring rod is now removed and wiped with moistened ashless filter paper, the latter is added to the oil, and the stirring rod is put in the beaker in which the titration is to be made. The residue is again heated until the filter paper is ashed, and then oxidized with 3 to 5 drops of 30 per cent neutral hydrogen peroxide. The ash is now heated to a dull red heat, covering the dish to prevent loss by spattering. If not practically free from carbon, the treatment with peroxide is repeated. After cooling, the dish is covered with water in a 250-cc. beaker and brought to a boil. It is now titrated in the presence of methyl orange with 0.5 *N* sulfuric acid, then about 0.5 cc. excess added, and boiled about 5 minutes to expel carbon dioxide. Half normal caustic is now added until slightly but distinctly alkaline, the dish and small stirring rod removed, and the titration finished as given under Fixed Alkalinity. The combined sulfate is given by the following formula, where *Al* represents total milligrams of alkali and *Ac* the amount of acid added or used during the titration:

$$\text{Combined SO}_3, \% = \left(\frac{Al - Ac}{\text{sample}} + A_F \right) \frac{8}{56.1}$$

DISCUSSION

Where the fatty acids in the oil have been neutralized with ammonia only, the oil will evidently contain no titrable fixed alkali. Moreover, part or all of the organically combined sulfate may have been neutralized with ammonia. In that case, upon boiling with caustic soda the ammonium sulfonate is converted into the sodium salt, with the liberation of ammonia and absorption of fixed alkali that can no longer be determined by titration. The fact that the fixed alkali is absorbed by the sulfonic group in this manner is indicated by a negative result obtained by means of the alkalinity formula, which should be carefully retained for use in subsequent calculations.

The writer finds that sodium acetate may be titrated with a fair degree of accuracy with thymol blue as the indicator. The pH (*f*) of 0.2 molal sodium acetate is 8.3, the same concentration of acetic acid is 2.86, and the color change of thymol blue is 1.2 to 2.8 (red to yellow). Since the pH of acetic acid is above the pH of the color change of thymol blue, it can exert only a very slight effect on the indicator. Hence NaAc may be titrated with thymol blue the same way as soap is titrated in the presence of methyl orange. However, the end point in the former case is not so sharp as might be desired.

The least accurate factor in the method is the titration, which may vary by as much as 0.1 cc. of half normal solution, or 2.8 mg. This affects the result on a one-gram sample by $2.8 \times 8/56.1$, or 0.4 per cent sulfate. By increasing the size of the sample taken for analysis, the error is correspondingly reduced. With a 5-gram sample, the accuracy of the method

is approximately 0.1 per cent sulfate, which is about the variation found in the data given below. It must also be evident that errors due to mechanical losses are smaller the less the excess of alkali added to the oil, the losses being a minimum or zero where there is no excess alkali present at all. It seems that excess alkali is not required in order to get accurate results. A number of tests were made with excess alkali varying from zero to an amount equivalent to twice the sulfate content, with practically identical results.

EXPERIMENTAL RESULTS

A number of analyses for organically combined sulfate in commercial sulfonated products by the old and new titration methods are given in Table I.

TABLE I. ORGANICALLY COMBINED SULFATE IN SOME COMMERCIAL SULFONATED OILS AND SALTS

SAMPLE	DESCRIPTION	ORGANICALLY COMBINED SO ₃	New method	
		Old method	%	%
1	Sulf. olive oil	4.90	5.28	5.29
2	Sulf. castor oil	5.09	5.41	5.47
3	Sulf. castor oil ^a	3.30	3.41	3.39
4	Sulf. neat's-foot oil ^b	1.87	2.08	2.01
5	Sulf. cod oil ^c	3.44	3.51	3.49
6	Sulf. oil ^d	8.92	9.48	9.48
7	Silk finishing oil	4.82	5.09	5.00
8	Silk soaking oil	1.97	2.10	2.14
9	Sulf. mineral oil ^e	..	Neg.	Neg.
10	Isobutyl naphthalene sodium sulfonate ^e	..	Neg.	Neg.

^a Completely neutralized with caustic soda.

^b Contained 0.88% NH₃, mostly as ammonium sulfonate.

^c Contained 1.45% NH₃, mostly as ammonium sulfonate.

^d Highly sulfonated oil of foreign manufacture.

^e Large amounts of sulfide formed on ashing.

ADVANTAGES OF THE NEW METHOD

The ash-titration method offers the following advantages over the old acid-boiling titration method: It is more rapid, particularly where many such analyses are made simultaneously, gives better check results, and requires fewer reagents. Moreover, the results are consistently higher, indicating either more complete decomposition than by the acid-boiling methods (titration and gravimetric), or the presence of true sulfonic acids. In this connection it is interesting to note that De Groote, Keiser, Wirtel, and Monson (2) report that the values for organically combined sulfate determined by the Parr bomb were much greater in some cases than results obtained by any method depending on decomposition by boiling, even for excessive periods, with mineral acid, such as concentrated hydrochloric acid. A sample of a true sulfonic acid of a saponifiable oil not being available at short notice, this phase was not further investigated. It was found, however, that the new method is not applicable to sulfonic acids that are not saponifiable, for example, sulfonated mineral oils, naphthalene sulfonic acid, etc. By taking a small sample for analysis, such as one gram, the method is sufficiently rapid to be used as a qualitative test for organically combined sulfate.

ACKNOWLEDGMENT

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Identification of Common Carbohydrates

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THOUGH some two hundred tests (9) for glucose, including different reagents with modifications of conditions, etc., are found in the literature, no one of these is exclusively characteristic for glucose and, indeed, no one physical constant will identify it. Some of the common carbohydrates, such as levulose, starch, mannose, glycogen, and cellulose, can be identified by a single test, but most of the others require two or more tests for reliable identification.

This study was undertaken to develop new tests for certain carbohydrates, to determine the extent of application of old tests, and to formulate a system of identification, based largely on color reaction, of the carbohydrates given in the table. Also an unsuccessful search was made to find a characteristic test for glucose.

A number of conditions have contributed to confusion in the identification of carbohydrates. First, numerous tests have been applied to individual carbohydrates,¹ but most frequently they have not been applied to all common carbohydrates, hence cannot be held to be characteristic. For example, nitroprusside (14), permanganate (1, 2), ferri-

¹ The application of the following reagents, given in the literature as characteristic for glucose, were applied to other carbohydrates and were found to be reactive with many other carbohydrates: mercuric, lead, uranium, vanadium, zinc, ferric, and tin salts; the cresols, naphthols, menthol, thymol, diresorcinol, and nitroso- β -naphthol; dyes such as methylene blue, alizarine red, saffranine, and indigo carmine; amino compounds such as the naphthyl amines, the hydrazines, benzidines, and the phenylene diamines, HBr and HI.

cyanide (3, 6), chromate (7, 12, 13), etc., have been used for glucose, and hydrochloric acid (10, 15) has been applied to levulose. The effects of these and other reagents on many carbohydrates are indicated in Table III.

Another cause of confusion has been the multiplicity of reagents applied and assumed to be characteristic, especially as applied to glucose and levulose. Many are modifications of the same reagent—there are six modifications of Seliwanoff's, ten of Nylander's, and ninety of Fehling's reagents.

TABLE I. GROUP IDENTIFICATION OF FRUCTOSE, SUCROSE, RAFFINOSE, AND INULIN (F)

IN DIL. HCl	TIME ELAPSED HEATED AT 100° C.	TIME READING	COLORS OF (F)	COLORS OF OTHER CARBOHYDRATES
	Min.	Min.		
TiCl ₄	2-5	5-20	Deep amber	Agar-agar faintly yellow
Phloroglucinol	20-30	5-20	Fructose, red-brown; others, deep amber	All colors deepened by NH ₄ OH
Orcinol	15-20	5-20	Raffinose amber; others, yellow	With NH ₄ OH (F) violet-red
Resorcinol	2-5	5-20	Cherry-red	Dextrin, maltose, glycogen, faintly yellow
Benzidine	2-5	5-20	Yellow-amber	Rhamnose, agar-agar, maltose faintly yellow
SnCl ₂	2-5	5-20	Amber to deep red	

Finally, some of the tests given are characteristic for impurities in the material tested. For example, cobaltous chloride (11, 13) was claimed to be a test for sucrose; we find that it is characteristic for levulose only.

TABLE II. REAGENTS

REAGENT	SOLVENT	AMT. OF REAGENT %	TIME HEATED AT 100° C. Min.	ELAPSED TIME READING Min.	REMARKS
a Water	a				Cellulose insoluble
b I + KI	H ₂ O	3	Heat to expel free iodine; cool
c Nylander's ^b	8% NaOH	6	1	1-5	Reagent catalyzed with AuCl ₃ ; (+) bk. ppt's.; (wh) white ppt's.
d Disch's	c		30	30+	Pentoses brown; hexoses, etc., blue
e Orcinol	d		1	1-5	See Table III
f Phloroglucinol	e		1	1-5	See Table III; boiling gives ChR with pectin, gum arabic, and gum tragacanth
g Na ₂ CrO ₄	H ₂ O	10	1	1-60	Simple sugars green; pectin, red solution
h Sodium nitroprusside	H ₂ O	1	1+	?	Add NH ₄ OH and heat; (+) green while hot; arabinose green without NH ₄ OH
i KMnO ₄	H ₂ O	0.1	..	1-60	(+) immediate decolorization; (*) decolor. in 1 hr.
j Fehling's ^c	H ₂ O		..	60	
k K ₃ Fe(CN) ₆	H ₂ O	0.5	1	1-5	+ FeCl ₃ ; brown, negative; greens, positive; maltose, blue
l Picric acid	H ₂ O	Sat.	1	1-5	+ NH ₃ ; nos. indicate depth of colors (red)
m H ₃ PO ₄	H ₂ O	85	1	1-60	Yellow to amber to brown to black; nos. = depth of colors
n HClO ₄	H ₂ O	60	1	1-60	Yellow to amber to brown to black; nos. = depth of colors
o H ₂ SO ₄	H ₂ O	50	1	1-60	Yellow to amber to brown to black; nos. = depth of colors
p HCl	H ₂ O	20	1	1-60	Nos. = depth of color; pectin, yellow
q KOH ^d	H ₂ O	5	1	1-60	Add carbohydrate, then 1/2 the vol. conc. H ₂ SO ₄ . Nos. = depth of color; rhamnose, green
r (NH ₄) ₂ MoO ₄	H ₂ O	5	..	60	Evap. 2/3 for mucic acid
s HNO ₃	H ₂ O	25	Nos. = depth of red
t H ₂ SeO ₃	50% H ₂ SO ₄	10	1	1-60	Nos. = relative speeds of decolorization of Ni ₂ O ₃
u Ni ₂ O ₃	h		Mostly ambers to brown-blacks ⁱ
v Heroine	H ₂ SO ₄	1	..	15	Mostly rose to brown-blacks ^j
w Codeine	H ₂ SO ₄	1	..	15	(+) black ppt. or silver mirror; some give brown solution
x AgNO ₃	Dil. NH ₄ OH	1	1	1-60	Boiling gives for (+) dichromate color; levulose and sucrose give color and ppts.
y p-Tolylhydrazine	Dil. HCl	1	..	1-60	

Table I

^a Mono-, di-, and trisaccharoses are sweet and soluble in cold water. Polysaccharoses, except cellulose, dissolve in hot water. Starch, pectin, glycogen, and gum tragacanth dissolve in hot water to give opalescence and foam. Gum arabic gives clear solution and foam. Dextrin and inulin give clear solutions but no foam.

^b Nylander's reagent: 2 grams of bismuth subnitrate and 4 grams of Rochelle salt dissolved in 100 grams of 8% NaOH.

^c Prepare 10% solution of diphenylamine in alcohol and add 1 volume to 4 volumes of acetic acid and 5 volumes of HCl (4).

^d To 5 cc. of saturated aqueous solution of orcinol, add 50 cc. of HCl and dilute to 90 cc.

^e To 0.2 gram of phloroglucinol in 10 cc. of alcohol, add 50 cc. of HCl and dilute to 90 cc. Solution of orcinol or of phloroglucinol in dilute HCl will indicate carbohydrates containing levulose. See Table I.

^f Fehling's reagent: (1) solution of 36.44 grams of CuSO₄·5H₂O in water diluted to 500 cc.; (2) solution of 125 grams of KOH and 173 grams of sodium potassium tartrate in water diluted to 500 cc.

^g Usually called Moore's test.

^h Prepare solutions (a) 10 grams of NiSO₄·7H₂O in 1000 cc. of H₂O, and (b) 4.8 grams of K₂S₂O₈ and 6 grams of KOH in 1000 cc. of H₂O. Use equal parts and let stand—black Ni₂O₃ precipitates. Carbohydrates decolorize this.

ⁱ With varied times and temperatures carbohydrates give changing colors. A check with a known carbohydrate is revealing and desirable. Perhaps in these reactions, formaldehyde is split off, because colors closely follow Kobert's (5, 8) test for codeine, etc.

TABLE III. EFFECTS OF VARIOUS REAGENTS ON CARBOHYDRATES

	CARBOHYDRATE	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p	q	r	s	t	u	v	w	x	y	z
1	Cellulose	—	—	—	Bl	—	—	—	—	—	—	Br	—	—	—	—	—	—	3	—	—	—	R	r	—	—	—
2	Starch	+	+	Wh	Bl	—	—	—	—	*	—	Br	—	—	—	1	—	—	—	—	—	—	—	r	—	—	—
3	Soluble starch	+	+	Wh	Bl	—	—	—	—	—	—	Br	—	rose	—	4	—	—	—	—	5	—	—	—	—	—	—
4	Glycogen	+	+	Wh	Bl	—	—	—	—	+	—	G	—	1	1	1	3	—	3	—	—	1	—	rV	Br	—	—
5	Dextrin	+	+	Wh	Bl	—	Am	—	—	+	+	G	—	—	—	2	—	5	—	—	1	3	—	—	Br	+	—
6	Pectin	+	—	—	Br	—	—	R	+	*	+	G	—	—	1	2	—	Y	—	+	1	1	—	—	Br	+	—
7	Levulose	+	—	+	Bl	Br	Br	+	+	*	+	G	9	9	9	9	9	9	9	—	9	4	Br	Br	+	+	+
							Bk															Bk	Bk				
8	Mannose	+	—	+	Bl	—	—	+	+	*	+	G	2	1	—	3	1	7	—	—	5	7	V	VP	+	—	—
9	Maltose	+	—	+	Bl	—	Y	+	+	+	+	Bl	2	3	1	5	—	8	6	—	3	9	Am	r	r	+	—
																								Br			
10	Rhamnose	+	—	+	Br	—	Or	+	+	—	+	G	2	2	3	6	—	4	G	—	3	4	orR	R	+	—	—
11	Arabinose	+	—	+	Br	Bl	ChR	+	+	*	+	G	9	1	2	2	—	7	7	—	8	8	r	R	+	—	—
12	Xylose	+	—	+	Br	Bl	ChR	+	+	*	+	G	9	1	—	7	—	7	5	—	7	8	r	R	+	—	—
13	Galactose	+	—	+	Bl	—	Am	+	+	+	+	G	2	1	—	3	—	7	—	+	6	5	—	—	+	—	—
14	Lactose	+	—	+	Bl	—	Am	+	+	—	+	G	2	—	—	3	—	7	6	+	6	2	—	—	+	—	—
15	Raffinose	+	—	—	Bl	Br	Br	—	—	—	—	Br	—	3	2	6	5	—	7	+	8	2	Am	Am	—	+	+
							Bk															Bk	Bk				
16	Sucrose	+	—	—	Bl	Br	Br	—	—	—	—	Br	—	8	8	8	7	—	8	—	8	2	Br	Am	—	+	+
							Bk															Bk	Bk				
17	Inulin	+	—	—	Bl	Br	Br	—	—	*	+	G	—	8	7	9	6	—	8	—	5	2	Am	r	—	+	+
18	Glucose	+	—	+	Bl	—	Y	+	+	*	+	G	2	—	—	3	—	8	—	—	2	6	—	—	+	+	—
19	Gum arabic	+	—	Am	Bl	—	—	—	—	+	+	G	—	3	2	6	—	3	2	+	5	1	r	—	—	—	—
					Bk																						
20	Gum tragacanth	+	—	Wh	Br	—	—	—	—	+	—	G	—	rose	1	4	—	—	4	+	6	1	R	R	—	—	—
					Bk																						
21	Agar agar	+	—	Am	Bl	Br	Br	—	—	—	—	G	—	—	4	4	3	5	8	+	—	—	BrR	vR	—	+	—
							Rk																				

Since most reagents used for identifying carbohydrates are not neutral, secondary effects are often produced. With alkalis, yellow to brown colors are developed; with acids, hydrolysis, caramelization, and carbonization result. Under properly controlled conditions of concentration, time, and temperature, these reactions become of great importance in identifying the carbohydrates. For example, if each of the carbohydrates is treated in the cold with 85 per cent phosphoric acid, only fructose blackens in 24 hours; when heated one minute in boiling water, fructose, sucrose, and inulin are indicated. However, if all are heated for a longer time, changes of color from faintly yellow through amber and brown to black result with all carbohydrates. Similar changes of color also result with other acids such as perchloric, sulfuric, hydrochloric, etc. However, under controlled conditions, the different rates of decomposition to yield color become valuable for indicating many of the carbohydrates.

Many of the reagents employed for carbohydrates are oxidizing;² toward these levulose shows the greatest ease of oxidation. However, all carbohydrates do not show the same order and rates of oxidation with different reagents. For example, maltose is more easily oxidized by nickelic oxide than galactose; the latter is more easily oxidized by silver nitrate.

With cold solutions, or with solutions heated one minute, and with readings made over extended times, rates of oxidation, hydrolysis, color formations, etc., can be read and their variations indicate the different carbohydrates. Increasing numbers in Table III show increased depth of color for equal times.

To identify some of the carbohydrates, the judgment of color can be confirmed by a repetition of the test on the unknown with another tube containing the suspected known carbohydrate, both materials being treated with the reagent in equal concentrations, temperatures, and times.

ONE-TEST IDENTIFICATION OF CERTAIN CARBOHYDRATES

1. CELLULOSE. Insoluble in hot water.^a
2. STARCH. Blue with iodine.^b Soluble starch is soluble in cold water.
3. GLYCOGEN. Wine-colored with iodine.^c Characteristic colors developed when glycogen is heated in dilute hydrochloric acid with certain ortho-diphenolic compounds and solution is made ammoniacal: catechol, deep brown-

² The term "reducing sugar" has been applied to Fehling's and other reagents. However, it is a misnomer because with some reagents all simple sugars are not oxidized, and with other reagents all carbohydrates and even mannitol are oxidized, as, for example, with nitric acid. Mannitol gives negative tests with most of the reagents of the table.

red; pyrogallol, deep brown; gallic acid, cherry-red; tannic acid, deep wine-red. Indigo colored solution of diphenylhydrazine HCl changed at ordinary temperature to permanganate color.

4. DEXTRINE (erythrodextrin). Red-violet to red-brown with iodine. With Nylander's reagent, whose alkalinity has been partially neutralized with hydrochloric acid, amber solution to white colloidal precipitate^d to black.
5. PECTIN.^e Sodium chromate develops color of dichromate. Cold 5% KOH gives bright yellow.
6. LEVULOSE. Heated with dilute cobaltous chloride cooled and treated with little ammonium hydroxide, a violet to purple color^f is developed. Most of the reagents of Table III indicate characteristic tests for levulose.
7. MANNOSE. Violet to purple^g with reagents v and w.
8. MALTOSE. Blue with reagent k and^h red-brown with x.
9. RHAMNOSE. Greenⁱ with reagent r.

^a Soluble in Schweitzer's reagent; in warm 85% phosphoric acid catalyzed by ZnCl₂; in acetic acid and acetic anhydride (4 to 1) catalyzed by H₂SO₄ or by ZnCl₂; in 30% ZnCl₂ in conc. HCl. Water yields precipitates with these solutions.

^b Raw and soluble starch are distinguished by cold water. Gum tragacanth and some samples of dextrin contain starch. Blue with iodine is decolorized by boiling and restored by cooling.

^c Discharged by heat and restored by cooling. Warming with Nylander's reagent salts out colloidal glycogen.

^d Soluble in cold mixture and reprecipitated by heat.

^e With sucrose and organic acid it yields a jelly.

^f Green cobaltous hydroxide with other carbohydrates.

^g Reagent v more characteristic.

^h Confirm by other tests of Table III.

ⁱ Other carbohydrates give blue or colorless solutions.

The other carbohydrates require two or more tests for identification; these are indicated in Table III. Table I indicates tests for the levulose-containing carbohydrates, and Table II gives a list of the reagents and their characteristics.

Reagents d, e, f, v, and w indicate pentoses and pentose-containing carbohydrates. Reagent f gives cherry-reds with arabinose and xylose, but when boiled, pectin, gum arabic, and gum tragacanth also give the cherry-red. With v and w arabinose is a red which persists longer than with any of the other carbohydrates.

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Sulfite Digester for Research and Instruction

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CHEMICAL engineering laboratory equipment should be selected on the basis of usefulness. Too frequently, expensive apparatus to be used at best part time is purchased, whereas a slightly modified form would have lent itself to a variety of experiments. Conversely, a special piece may be purchased for a limited but important investigation and then with a few and relatively inexpensive accessories, used for basic studies in class work. In such cases, one can justify the initial expense. This discussion has to do with the design of a special KA 4 metal rotary digester for sulfite pulping studies, and also its use in class work.



FIGURE 1. DIGESTER SHOWING KA 4 METAL CASTING

The preparation of sulfite pulp in the laboratory is usually limited to working with heavy glassware and rare-metal containers. Such limitations frequently permit working with only small samples. At the University of Washington, a digester of 25 liters capacity has been in operation for several months, and because of the ease of control and wide limits of operation and application, a detailed description has been prepared. Those interested in such equipment may find use for this apparatus and many can add, no doubt, to its applicability.

In the digestion of wood chips by a solution, variables such as size and composition of chips, temperature, concentration, and composition of solution are usually studied. Uniformity of operating conditions is always desirable. Apparatus for such work should withstand corrosion, allow for simple but accurate control, be of the rotating or tumbling type, and externally heated.

DESCRIPTION OF DIGESTER

The digester is shown in Figure 1. The body of KA 4 metal was cast from the pattern of a standard 6-inch steel steam drip pocket. The flanged opening was fitted with stud bolts which, in conjunction with a solid KA 4 metal plug in the bottom, were used for mounting the casting in a steel drum. The side openings intended for gage cocks in the drip pocket were used for thermometer well, pressure gage, sampling, and blow-down fittings. The apparatus was given a 24.6 kg. per sq. cm. (350 lb. per sq. in.) hydrostatic test. Figure 2 shows the mounting of the casting in the steel cylindrical drum which rotates at right angles to its axis. The sprocket, chain drive, and commutator rings for electrical heating are evident. Two steel digesters similar

to the one described are installed and all may be rotated from a main drive at 4.7 r. p. m.

The speed of rotation is not so great but that temperatures and pressures may be read without stopping the apparatus. Three electrical resistance coils, which are used for heating, are connected through three commutator rings, and hence no switches need be on the rotating drum. There is little danger of heating interruptions due to shorting with this arrangement.

OPERATION

Before use of this digester for sulfite pulping studies, two series of heating rates were obtained. One was made with the KA 4 digester insulated only with the electrical packing normally placed around the heating elements and in running position. The other was obtained after packing "85 per cent magnesia" between the digester and the steel carriage. In these runs 18 kg. (39.6 lb.) of water were heated. The results, given in Figure 3, show that 0.56 kw. maintained a

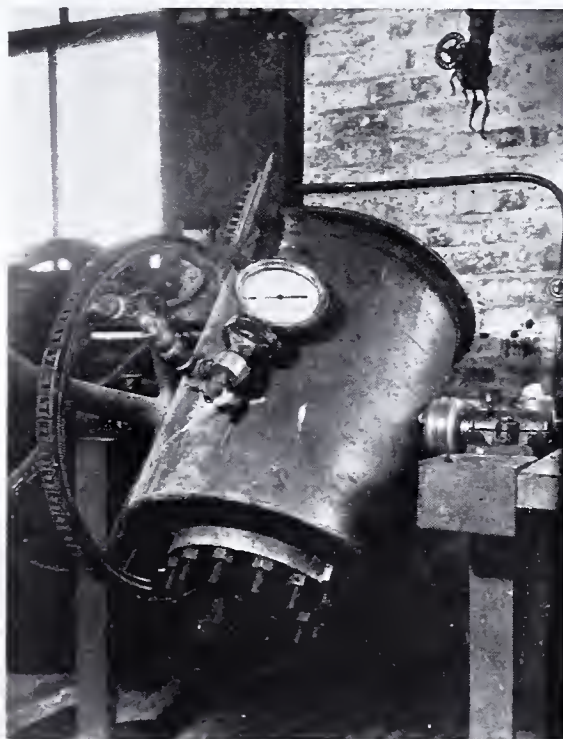


FIGURE 2. ASSEMBLY OF DIGESTER

constant temperature of 132° C. (270° F.) before and 146° C. (295° F.) after packing with 85 per cent magnesia. The usual maximum temperatures used in the sulfite cooking process are 143° to 149° C. (290° to 300° F.). The additional insulation had little effect upon the rate of temperature rise to 149° C. (300° F.) when 2.07 and 1.12 kw. were used.

EXPERIMENT IN RATE OF HEATING

Charges may be heated having heat capacities other than that equivalent to 18 kg. of water, and then the heating

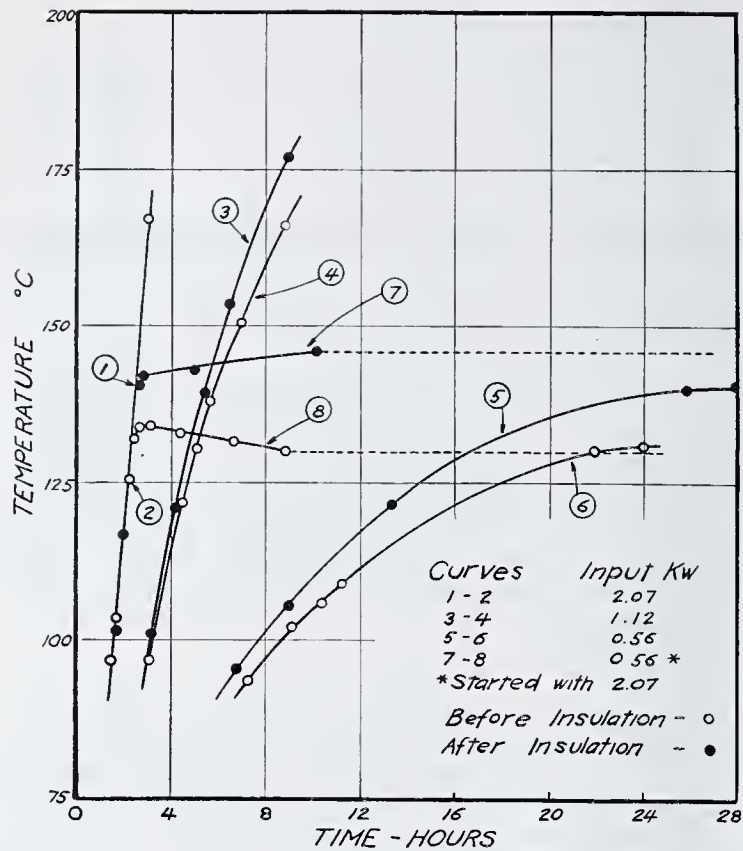


FIGURE 3. DIGESTER HEATING RATES

time required to bring to a given temperature is desirable. A method for such calculations is given below. Assuming that each temperature represented on the 2.07-kw. input curve of Figure 3 gives the average temperature of the metal digester and the water, the total heat loss, Q_2 , in lagging and radiation up to a given time, Θ hours, is given by:

$$\frac{(1000)(2.07)(3600)\Theta}{4185} = \left[\frac{(22.7)(454) + w}{1000} \right] (T - T_r) + Q_2 \quad (1)$$
$$\frac{(1000)(2.07)(3600)\Theta}{1055} = (22.7 + w)(T - T_r) + Q_2 \quad (1a)$$

The total heat capacities in Calories per °C. or B. t. u. per °F. of the metal parts and of the water are $(22.7)(454)/1000$, or 22.7 and w , respectively, depending on the units. Equation 1 is for metric and 1a for English units. Room temperature, T_r , is taken as 25° C. (77° F.), while T represents the average temperature of the water. Corresponding values of time and temperature have been taken from curve 1 of Figure 3, and Equation 1 solved for Q_2 . Values of Q_2 so calculated have been plotted against $T - T_r$ on log-log paper and result in the equation:

$$Q_2 = 2.45 (T - T_r)^{1.35} \text{ in metric units}$$
$$Q_2 = 4.40 (T - T_r)^{1.35} \text{ in English units}$$

where T_r is the room temperature and Q_2 is expressed in Calories or B. t. u., respectively. Substituting this value of Q_2 in Equation 1 and simplifying,

$$\Theta = (0.00578 + 0.00000056 w)(T - T_r) + 0.000137(T - T_r)^{1.35} \quad (2)$$
$$\Theta = (0.00321 + 0.000141 w)(T - T_r) + 0.000622(T - T_r)^{1.35} \quad (2a)$$

where Θ represents the hours required to heat a charge of w grams or pounds of water from 25° to T ° C. (77° to T ° F.). In Figure 4, Equation 2 has been solved for values of w equal to 5 and 10 Calories per °C. (11.0 and 22.0 B. t. u. per °F.) corresponding to charges of 5 and 10 kg. (11.0 and 22.0 lb.) of water. Experimental results for such charges are also indicated in Figure 4. The maximum error intro-

duced in calculating by means of Equation 2 the time required to heat 10 kg. (22.0 lb.) of water from 25° C. (77° F.) to any temperature below 149° C. (300° F.) is illustrated by selection of the temperature 164° C. (327° F.). The error for this temperature is 9.0 minutes, or 6 per cent. Similar calculation for a charge of 5 kg. (11.0 lb.) of water shows the same error.

MEASUREMENT OF HEAT LOSSES

When the temperature of the digester charge becomes steady, and after allowing for the energy required for any change taking place, the electrical input will be equivalent to the heat losses. Measurement of such losses can be accomplished easily with the usual electrical meters. Since heat leaves the steel jacket by radiation and convection,

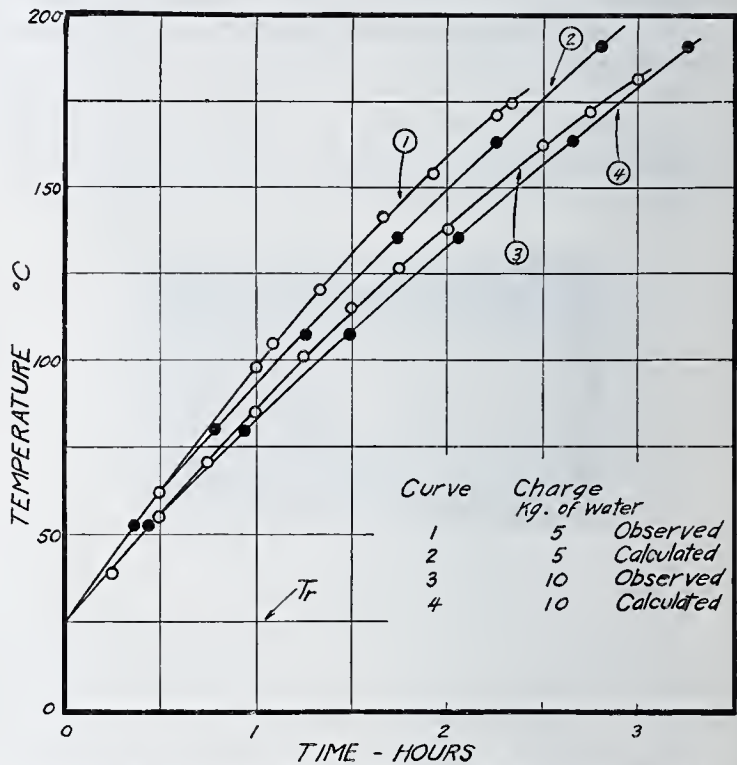


FIGURE 4. COMPARISON OF CALCULATED AND OBSERVED HEATING RATES

the quantitative determination of either loss separately is rather complicated, and simplifying expressions have been suggested. Although the transfer of heat by radiation from a body is proportional to the fourth power of its absolute temperature, the net exchange between two bodies at approximately room temperature, having a small temperature difference, may be approximated closely by assuming it proportional to only the temperature difference as in heat transfer by conduction. Heat transfer due to radiation and convection may be estimated from the equation

$$\frac{Q}{\Theta} = (hc + hr)A \Delta T \quad (3)$$

where $\frac{Q}{\Theta}$ = heat transferred per unit of time
 $hc + hr$ = gas film + radiation coefficient
 A = area of hot body
 ΔT = temperature difference

The application of this equation in work with the digester can be exemplified by measuring the heat input required for maintaining steady charge temperatures and recording the temperature of the steel-jacket surface and of the room. An input of 0.56 kw. (481 Calories per hour) was found to maintain the temperature of the charge at 146° C. (295° F.). The skin temperature of the steel jacket averaged 45° C.

(113° F.) and that of the room 25° C. (77° F.). The value of $(hc + hr) A$, using Equation 3, is found to be 24.1 Calories per hour per °C. (53.2 B. t. u. per hour per °F.).

Heat capacities of solutions and mixtures, in particular those used in the pulping industries, can be determined by the use of Equation 1.

CHEMICAL PREPARATIONS

Undergraduate laboratory courses in industrial chemistry have many uses for rotating autoclaves. The preparation of wood pulp is but one of the digestion processes which

familiarize the student with important phases of the chemical industry. Other processes, especially those peculiar to geographical location, suggest themselves.

The object of this paper has been to show that expensive research equipment can be also used for undergraduate instruction in industrial chemistry and chemical engineering. The intensive and general application of apparatus can justify the installation of equipment developed for special investigations.

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Estimation of Thallium after Oxidation with Bromine

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OF THE reagents employed for the oxidation of thallium, bromine has received little attention, although its action is rapid and complete. Sponholz (3) recommended it for the volumetric estimation of thallium, using the color of excess bromine to indicate when the reaction was complete. In the description of this method he called attention to the necessity of frequent standardization of the bromine solution. The difficulties of such a volumetric procedure are quite obvious. If, however, the oxidized solution is treated with an alkali hydroxide in slight excess, the immediate and complete precipitation of thallic hydroxide is effected.

The delicacy of this reaction was first tested qualitatively, and it was found that in a volume of 10 cc., 0.1 mg. of thallium could be detected by the dark coloration of the thallic hydroxide, a delicacy which was rarely exceeded by such reagents as potassium iodide, chloroplatinic acid, or sodium cobaltinitrite. Sodium peroxide proved to be much less satisfactory as a means of detection. This test cannot be made in the presence of such elements as iron, manganese, cobalt, or nickel which give similar color changes due to oxidation.

Quantitatively the results were as follows: A solution of thallic nitrate was made up and standardized by oxidizing four portions of 10 cc. each with potassium ferricyanide in the presence of potassium hydroxide (1, 2), filtering off the thallic hydroxide on a weighed asbestos felt, and weighing the oxide after bringing it to constant weight at a temperature

of 150° to 200° C. The mean of four closely agreeing results gave 0.1345 gram of thallic oxide.

Portions of 10 cc. each of this same solution were oxidized with bromine water in slight excess, the oxidized solutions precipitated, with or without gentle warming, with sodium or ammonium hydroxide, and the precipitates filtered off, heated, and weighed in the same manner as the precipitate from the ferricyanide treatment described above. Four closely agreeing results, ammonium hydroxide having been used as the precipitant, gave as a mean 0.1334 gram of thallic oxide; and another four, sodium hydroxide having been employed as the precipitant, gave a mean of 0.1344 gram of thallic oxide.

The method was rapid, easy of manipulation, and certainly, when sodium hydroxide was used, of satisfactory accuracy. Obviously, those elements whose hydroxides are insoluble in excess of sodium or ammonium hydroxide must be absent when this method is applied. This necessitates the previous removal of thallium from most of the other elements, a procedure not unusual before the application of many gravimetric processes to the estimation of a single element.

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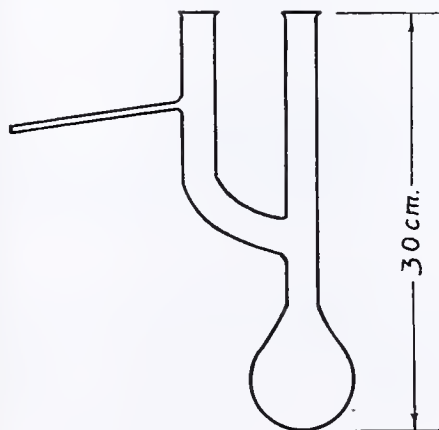
RECEIVED May 20, 1932.

An Improved Flask for Van Slyke Protein Analysis

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THE flask shown has been found to be an improved form for hydrolysis of proteins according to Cavett's modified Van Slyke nitrogen distribution method (1). It consists of a 300-ml. Kjeldahl flask to which has been attached a side neck, in the manner of a Claissen flask. Several operations are performed in the flask, saving time and increasing accuracy. The protein sample is hydrolyzed, the hydrochloric acid is distilled off, the ammonia nitrogen is determined, and the total nitrogen in the humin fraction is determined, all in the same flask on the same sample.

The advantages of this Kjeldahl-Claissen flask over the 250-ml. distilling flask recommended in the original method, are: (1) The double neck prevents foam from bubbling over into the standard acid during the ammonia determina-



tion. (2) The additional strength of the Kjeldahl flask makes it more suitable for the Kjeldahl digestion, etc.

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Detection of Gelatin in Dairy Products

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GELATIN has for many years been used as a thickening agent in dairy products. In ice cream it has of course been accepted because it improves the texture as well as the standing qualities of this product. However, in milk and cream and like products, its use has generally been frowned upon because of a tendency to use it to conceal inferior products.

The method mainly used for its detection in dairy products in the past has been that of Stokes (10), which will be described in detail later. This method, however, in the case of slightly soured milk or slightly soured sweet cream, and especially in the case of sour cream, fails to give a decisive result in the absence of gelatin. This necessitates either a laboratory rule-of-thumb method, such as the density of turbidity before considering a test positive, or a resort to a test distinguishing between a gelatin-picric precipitate and a pseudo-gelatin-picric precipitate such as the Seidenberg method (8). This test, besides being laborious, does not always differentiate between the aforementioned types of precipitate.

In view of these facts, the authors have developed a method from their experience with other thickeners (3) which will completely satisfy the condition of giving no precipitate in the case of a dairy product in which gelatin is absent and a heavy precipitate or a marked turbidity for every dairy product containing gelatin, including sour cream. Furthermore, this method needs no laborious confirmatory tests.

The properties of gelatin as a colloid have been discussed so frequently in the literature that there is no need for a further discussion along these lines here. However, there are many other properties of gelatin so little known and yet so pertinent to its detection that it would be wise to review them. Moreover, there are a few methods used for the estimation of gelatin which are also used for its detection which will be reviewed.

Trillat (12) estimated gelatin in gums and alimentary substances by weighing the precipitate produced by formaldehyde.

Henzold (2) boiled the material supposed to contain gelatin in water and filtered. The filtrate is boiled with excess 10 per cent potassium dichromate. After cooling, if gelatin is present, a few drops of concentrated sulfuric acid produce a white, flocculent precipitate.

Greifenhagen (1) used zinc sulfate to precipitate both gelatin and proteoses. The zinc sulfate precipitate is redissolved and reprecipitated by use of mercuric chloride. Since mercuric chloride precipitates the proteoses only, the filtrate will contain only gelatin, which can be estimated by determining the nitrogen.

A. and L. Lumiere and A. Seyewitz (6) made a series of studies of the properties of 10 per cent gelatin solutions. They found that it is precipitated by phosphotungstic and phosphomolybdic acids, chlorine and bromine water, and ferric, manganic, vanadic, ceric, uranic, and mercuric salts. They made a rather exhaustive study of the properties of

A method for the detection of gelatin in dairy products, especially for sour cream and cultured milks, is presented. Basic lead nitrate is used as a protein precipitant and calcined charcoal is used to adsorb the pseudo-gelatins formed in the souring process. The details of the method and its comparison with other methods as to sensitivity and applicability are given. It is found less sensitive but more definite than the official or Stokes method.

concentrated solutions of gelatin.

Steinizer (9), in a study of the properties of gelatin and glue in comparison with other proteins, noticed that lead acetate solution did not precipitate gelatin, whereas it did precipitate chondrins and mucins.

Straub (11) states that if gelatin solution is shaken for 20 to 30 minutes with a few cubic centimeters of thionin solution,

a dark blue color results, whereas if agar-agar is treated the same way, a violet coloration is obtained.

Liesegang (5) found that if 40 per cent tertiary potassium phosphate and 10 per cent cupric chloride are allowed to diffuse into gelatin gel, the green tertiary cupric phosphate does not result, but a deep violet transparent color. A water-gelatin solution may be used as well, but tertiary potassium phosphate causes a precipitate of gelatin. However, in 1914 (4) he pointed out that tricalcium phosphate and cupric chloride gave a violet color without turbidity instead of a green precipitate in the presence of gelatin in solution.

STOKES METHOD

The official method given in the methods of the A. O. A. C. for the detection of gelatin in milk and milk products is the Stokes (10) method. This is performed in the following manner: To 10 cc. of milk or cream or milk product, add an equal volume of acid mercuric nitrate solution (mercury dissolved in twice its weight of nitric acid and this solution diluted to 25 times its volume with water). Shake the mixture, add 20 cc. of water, shake again, allow to stand 5 minutes, and filter. If much gelatin is present, the filtrate will be opalescent and cannot be obtained clear. To a portion of the filtrate contained in a test tube, add an equal volume of saturated aqueous picric acid solution. A yellow precipitate will be produced in the presence of any considerable amount of gelatin, whereas smaller quantities will be indicated by a cloudiness. In the absence of gelatin, the filtrate will remain perfectly clear.

Acid mercuric nitrate is added to the milk product in order to precipitate all the proteins except gelatin. In the souring process certain decomposition products are formed whose exact nature is unknown. Patrick (?) found that these substances had properties very similar to gelatin, and called them "pseudo-gelatins." They are not completely precipitated by acid mercuric nitrate, and they give a precipitate with picric acid and with tannic acid. Consequently, the Stokes method is indeterminate for milk and sweet cream on the verge of souring, and fails completely for sour cream. Furthermore, acid mercuric nitrate itself will, if present in large excess, cause a turbidity in the presence of picric acid, and a turbidity will develop on standing even if the acid mercuric nitrate is not in excess.

SEIDENBERG METHOD

Seidenberg (8) developed a method to distinguish between the precipitate produced by gelatin and that produced by

pseudo-gelatin. His method is as follows: After performing the Stokes test, shake the solution and precipitate in a large test tube very thoroughly, allow to stand, decant off the clear liquid, and collect the precipitate on a filter. Wash with water containing 2 to 3 drops of ammonia per 100 cc. until the washings are slightly alkaline to litmus, then with water alone until they are neutral. Transfer the precipitate or the precipitate and filter to a small beaker, add 10 to 20 cc. of water, heat to boiling, and filter hot into a test tube. The filtrate will contain the gelatin-picric but not the protein. Cool and test for gelatin by adding an equal volume of the picric acid solution.

This method was advocated for sour creams, but failed to solve the problem completely because sometimes on samples known to contain gelatin, a positive test for gelatin with picric acid was not obtained after subjecting the sample to the Seidenberg treatment.

BASIC LEAD NITRATE METHOD

In view of the limitations of both the Stokes and Seidenberg methods, the authors have devised and developed an entirely new method for the detection of gelatin in dairy products. This method is based on the separation of gelatin from the other proteins in the milk product and then the subsequent identification of gelatin. This is done first by the use of a protein precipitant, and second by the use of an agent to adsorb the pseudo-gelatins and proteoses. The protein precipitant is basic lead nitrate and the adsorbing agent is calcined charcoal. The basic lead nitrate consists of two solutions added separately to the solution or mixture to be clarified.

Solution 1: lead nitrate, 250 grams to 500 cc.

Solution 2: sodium hydroxide, 25 grams to 500 cc.

To 10 cc. of milk or milk product, add 3 cc. of lead nitrate solution and stir, add 3 cc. of sodium hydroxide solution and stir, add 5 cc. of water and stir, add 0.1 gram of calcined charcoal and stir thoroughly, allow to stand for 5 minutes, and filter. To 3 cc. of the filtrate add 2 drops of concentrated nitric acid and then a few drops of freshly or recently prepared 5 per cent tannic acid solution. In the presence of gelatin there is a white or brownish voluminous precipitate. In the absence of gelatin the solution remains perfectly clear. As a confirmatory test, add to a portion of the filtrate (no addition of nitric acid is now necessary) an equal volume of freshly filtered saturated aqueous picric acid solution. In the case of considerable quantities of gelatin, there is a heavy precipitate of gelatin picrate. In the case of smaller quantities, there is a turbidity which develops within 2 minutes. In the absence of gelatin, the filtrate will remain perfectly clear even on standing. For the tannic acid test the addition of nitric acid is essential, for otherwise tannic acid will always give a precipitate. For the picric acid test there is no need to use acid. The addition of acid in this case reduces the sensitivity of the test, because gelatin picrate is somewhat soluble in nitric acid.

BASIC LEAD ACETATE METHOD

As an alternative method to the one given above, the authors suggest the following. It will not give as good results as the previous method, but nevertheless is better for sour creams than the Stokes method. It is based on the same principle as the preceding one, but uses dry basic lead acetate instead of basic lead nitrate solution as the protein precipitant. The adsorbing agent used is the same. The dry basic lead acetate may be made in the manner given in the methods of the A. O. A. C. or in any sugar handbook.

To 10 cc. of milk or milk product, add 1 gram of basic lead

acetate and stir. Add 15 cc. of water and stir, add 0.1 gram of calcined charcoal and stir thoroughly, allow to stand for 5 minutes, and filter. To 3 cc. of the filtrate add 3 cc. of water, 2 drops of concentrated nitric acid, and then a few drops of freshly or recently prepared tannic acid. A heavy voluminous white or brownish precipitate shows the presence of gelatin. To another portion of the filtrate add an equal volume of water and 2 to 3 drops of concentrated nitric acid, and then add an equal volume of freshly filtered saturated aqueous picric acid solution. A heavy precipitate of gelatin picrate or a pronounced turbidity which develops in 2 minutes shows the presence of gelatin. In the absence of gelatin the filtrate will remain clear for at least 10 minutes. The main drawback of this method is that after adding picric acid, a crystalline precipitate settles out on standing if the filtrate from the basic lead acetate treatment is not diluted. However, this precipitate is markedly different from gelatin picrate or pseudo-gelatin picrate, and consequently can easily be distinguished.

EXPERIMENTS ON ADSORBING AGENT

In order to determine the best adsorbing agent for the pseudo-gelatins a series of experiments were run with various adsorbents and clarifying agents. The results of these are given in Table I.

TABLE I. EXPERIMENTS TO DETERMINE ADSORBING AGENT

(All results considered after 2 minutes)

ADSORBENT	PICRIC ACID		TANNIC ACID	
	Sour cream without gelatin	Sour cream with gelatin	Sour cream without gelatin	Sour cream with gelatin
Fuller's earth	Clear soln.	Ppt.	Faint ppt.	Heavy ppt.
Magnesium carbonate	Turbid	Turbid	Ppt.	Heavy ppt.
Calcined charcoal	Very clear soln.	Ppt.	Very clear soln.	Heavy ppt.
Kaolin	Turbid	Ppt.	Heavy ppt.	Heavy ppt.
Pumice	Ppt.	Ppt.	Heavy ppt.	Heavy ppt.
Blood charcoal	Clear soln.	Turbid	Faint ppt.	Heavy ppt.
Alumina cream	Ppt.	Ppt.	Heavy ppt.	Heavy ppt.

These tests were performed in the following manner: Sour cream known not to contain gelatin was subjected to the basic lead nitrate treatment substituting in each case 0.1 gram of the adsorbents given in Table I. Columns 1 and 3 show the results with picric and tannic acids. Then sour cream known to contain gelatin was again tested by the basic lead nitrate method, substituting in each case 0.1 gram of each adsorbent. These results are shown in columns 2 and 4. It can be seen at a glance that calcined charcoal adsorbs the pseudo-gelatins the most, and gelatin itself the least, making it ideal for use in this test. The authors found that decolorizing carbons were better adsorbents to use in this test than carbons used for physiological or pigment purposes. Of these types of decolorizing carbons, Eimer and Amend's calcined charcoal, Darco, and Norit were found to be about equally efficacious as the adsorbing agent.

COMPARISON OF METHODS

SENSITIVITY. The basic lead nitrate method will give a good test for gelatin for one part of gelatin in 2000 of the milk product. The actual sensitivity of this reaction is greater than one part in 2000 but, owing to the addition of the adsorbing agent, it is lowered. This is compensated by obtaining an exceedingly clear filtrate and negative test. Moreover, this disadvantage is completely balanced by the fact that the use of gelatin in dairy products requires a greater proportion than one part in 2000 if the effect the gelatin is supposed to produce is really to be obtained. However, the method is only sensitive to one part in 400 for such products as ice cream or ice cream mix, particularly if these products contain egg material.

TABLE II. COMPARISON OF METHODS FOR APPLICABILITY

(All tests considered after standing 2 minutes)

METHOD	REAGENT	SWEET CREAM		SOUR CREAM	
		Without gelatin	With gelatin	Without gelatin	With gelatin
Stokes	Picric acid Tannic acid	Very faintly cloudy Heavy ppt.	Heavy turbidity Heavy ppt.	Turbid Heavy ppt.	Heavy turbidity Heavy ppt.
Basic lead acetate	Picric acid Tannic acid	Very faintly cloudy Clear soln.	Marked turbidity Heavy ppt.	Very faintly cloudy Clear soln.	Marked turbidity Heavy ppt.
Basic lead nitrate	Picric acid Tannic acid	Perfectly clear soln. Perfectly clear soln.	Turbid Heavy ppt.	Perfectly clear soln. Perfectly clear soln.	Turbid Heavy ppt.

In order to make certain as to whether this method would detect any type of gelatin, twenty samples of gelatin of various grades and types, one sample of glue, and one sample of isinglass were respectively incorporated with sour cream, or milk or cultured milks which had previously been found not to contain gelatin. Subjecting these prepared samples to the basic lead nitrate test yielded a positive test for gelatin for every type of gelatin or glue used. These tests were performed on sour cream samples containing 0.25 per cent gelatin.

A further series of experiments was run to determine whether time would alter the sensitivity of this test. This set of experiments at the same time reproduced plant conditions, for a dairy product to be tested for gelatin seldom comes directly to the analytical laboratory from its original source, hence time elapses before the test for gelatin is made.

To three samples of sour cream which had been found not to contain gelatin by the basic lead nitrate method three samples of gelatin were added. For each cream and each sample of gelatin, a 0.25 and 0.5 per cent mixture of gelatin in cream was made. These six prepared samples were tested for gelatin over a period of one month at various intervals. They continued to give a decisive test for gelatin throughout the entire period.

Practically every type of dairy product that might contain gelatin was tested by this method to determine whether it would apply in every case. The following products were tested: milk, sweet cream, sour cream, sweetened condensed milk, unsweetened condensed milk, and cultured milks. Ice cream samples were also tested and in every case gave a positive test for gelatin, as might be expected from the fact that nearly all ice creams contain gelatin. For unsoured ice cream and ice cream mix, the amount of adsorbent added and the length of standing time must be strictly adhered to in order to obtain results.

APPLICABILITY. The basic lead nitrate method was rigidly tested for complete and practicable applicability in three ways. First, it was compared with the Stokes method. This was done in the following manner: The Stokes method we know works for sweet creams. Consequently, a sweet cream known not to contain gelatin was tested by the Stokes, the basic lead nitrate, and the basic lead acetate methods. To a portion of this cream which was found negative for gelatin by all three methods, some gelatin was added, the sample was again tested by all three methods, and all three gave a positive reaction. Then that portion of the sweet cream to which no gelatin was added was allowed to sour. This soured cream was now tested for gelatin by all three methods. The Stokes test was now indeterminate because of a turbidity, the basic lead acetate method gave a very faint turbidity, whereas the basic lead nitrate method yielded a

perfectly clear negative result. Gelatin was now added to the remainder of the soured cream and was again tested by all three methods. The results of this experiment are given in Table II.

It may be seen in the table that the Stokes method gives a positive gelatin test with a soured sweet cream containing no gelatin. It may also be seen that the tannic acid test for gelatin cannot be used in conjunction with the Stokes method.

The second test of the basic lead nitrate method was performed in the following manner: Samples of cream and cultured milks containing and not containing gelatin were submitted to three chemists. These chemists did not know which samples contained the gelatin and which did not contain it. By the use of this method every sample of cream or of cultured milk with gelatin and those without it were reported correctly by each of the three.

The third test of this method was performed by subjecting various grades of gelatin and glue and isinglass to the test. These results have been discussed in the above text.

DISCUSSION

The basic lead nitrate method is one which, in so far as the picric acid reaction for gelatin is concerned, is less sensitive than the Stokes method, but which far surpasses the Stokes test in the following particulars:

1. It gives a perfectly clear blank or negative result in the absence of gelatin for sour cream and cultured milks, as well as for any other dairy product, for the reactions with tannic acid and picric acid.
2. The filtrate can be tested by one reagent—namely, tannic acid—and confirmed by another reagent—namely, picric acid.
3. It is easy to perform and dispenses with the Seidenberg addition to the Stokes test.

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Determination of Carbon in Fermented Liquors

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IN STUDIES involving the dissimilative changes of carbohydrates by microorganisms, it is desirable to control the analytical results by comparing the total carbon found by analysis in the medium, or in any fraction, with that represented by the various end products. Frequently, in fermentation studies, no attempt is made to account for the carbon in this manner, and it will be found by computation that the difference between the total carbon in the medium and the carbon accounted for in the final dissimilative products may range from 5 to 50 per cent of the carbon in the medium at the start of fermentation. There is difficulty when an organism produces relatively large amounts of gum, as this may contain sufficient carbon to endanger seriously any deductions concerning the scheme of dissimilation, unless taken into consideration. The advantages of a convenient and accurate method for the routine determination of total carbon in the medium are apparent. A determination of total carbon frequently saves considerable time when a fraction of the fermented medium is being examined, such as the neutral distillate or the nonvolatile acid residue. A determination of the carbon will immediately indicate whether all of the carbon is accounted for by the products isolated from the fraction. Other carbon products may have remained in the fraction and may thus have been overlooked.

Grey (5) was one of the first to apply this idea to the examination of fermented liquors. His method failed to effect complete combustion, although valuable information as to the nature of the organic compounds present could be obtained by it.

Friedemann and Kendall (4) and, independently, Heck (6) have developed the method based on the oxidation of the carbon to carbon dioxide by chromic acid. Friedemann and Kendall pointed out the necessity of maintaining a high concentration of acid during the oxidation by keeping the volume of water at a minimum. The carbon dioxide was absorbed by 0.5 *N* sodium hydroxide solution in a Truog tower (7), and the excess sodium hydroxide was titrated after the carbon dioxide had been precipitated by barium chloride. The method gives excellent results on solutions of pure organic compounds, but suffers because of the necessity of running a blank along with each determination. Considerable difficulty may be encountered in the titration when small amounts of carbon are being determined.

The impracticability of running a blank in actual practice is evident. Chlorides are usually present in culture media and are oxidized by hot chromic acid. A blank run does not always give a true indication of the amount of sulfuric acid fumes which may be absorbed.

A further necessity of running a blank results from the fact that very few samples of phosphoric acid can be found which do not contain carbon in some form. Quite often as much as 10 to 30 mg. of carbon has been found to be present in 30 cc. of phosphoric acid. Heck (6) avoided part of these difficulties by introducing a fume trap at the top of the reflux condenser.

The chief difficulty to be overcome, however, in the adaptation of any method for carbon determination to fermentation studies, is the necessity of maintaining a high acid concentration. Quite often the carbon-containing compounds are

present in such low concentrations that it is necessary to use as much as 200 cc. of the solution in order to obtain appreciable quantities of carbon dioxide. Oxidation with chromic acid is not complete in the presence of the quantity of water sometimes required (4).

Of the strong oxidizing agents, the only ones worthy of consideration under the circumstances are the chlorates, persulfates, and probably certain of the peroxides which act catalytically, such as silver peroxide. Of these, the chlorates are practically precluded because of their explosive tendencies, and because of the large quantities of chlorine which may be evolved. The peroxides either decompose too rapidly in water or are too expensive.

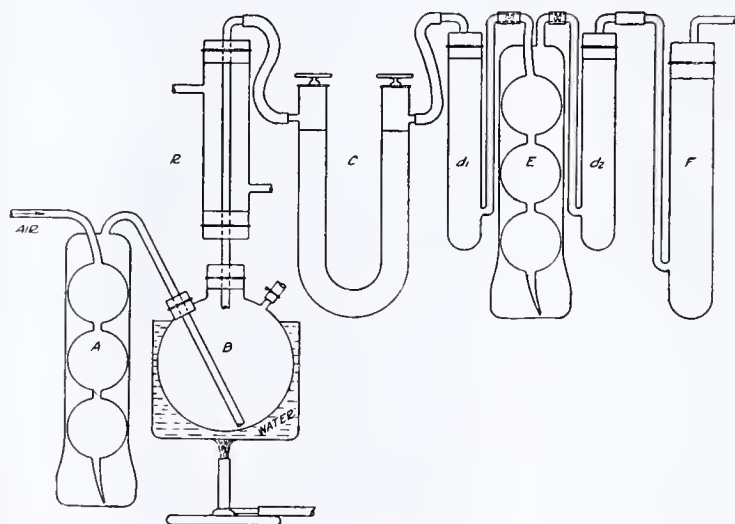


FIGURE 1

The only reference to persulfate oxidation of carbon which was found in the literature is that of Franz and Lutze (3). According to these authors, certain compounds, such as acetates, carbohydrates, and glycerol, can be quantitatively oxidized in dilute solution at 70° C. in the presence of three times the theoretical quantity of potassium persulfate. The available oxygen from potassium persulfate may be calculated from the equation $K_2S_2O_8 + H_2O \rightarrow 2KHSO_4 + O$. The oxidations were carried out in the presence of 100 cc. of water. The carbon dioxide was absorbed in potash bulbs and weighed. The presence of chlorides vitiated the results. The method as recorded by these authors has certain disadvantages which may be easily overcome.

METHOD FOR CARBON DETERMINATION

Aside from accuracy and rapidity, two requirements must be met if a routine method for the determination of carbon in fermentation liquors is to be successful.

1. The presence of water in quantities up to 200 cc. must not be objectionable.
2. The method must be applicable in the presence of mineral chlorides, and chlorine-, sulfur-, and nitrogen-containing compounds.

The method as described below has met these requirements satisfactorily.

METHOD. The oxidation is carried out in the presence of

180 to 200 cc. of carbon-free water by means of potassium persulfate. The carbon dioxide either may be absorbed in Bowen potash bulbs and weighed, or determined by any of the volumetric methods. In the present procedure, the carbon dioxide is weighed. Ordinary distilled water is freed from carbon and carbon dioxide by adding about 10 grams of potassium persulfate to 500 cc. of water, and distilling in the presence of a little silver nitrate as catalyst.

APPARATUS. The apparatus used is shown in Figure 1. The oxidation takes place in the 200-cc. balloon flask, *B*. The reflux condenser, *R*, need not be more than 10 inches (25 cm.) in length. The U tube, *C*, is filled with 12-mesh calcium chloride, with a few large pieces on top of the arm next to the condenser. The small calcium chloride tubes, *d*₁ and *d*₂, are also filled with 12-mesh calcium chloride, with larger pieces of the chloride placed next to the potash bulbs—i. e., in the bottom of each tube. The carbon dioxide is absorbed in the Bowen potash bulb, *E*. The bulb is filled with a 65 per cent solution of potassium hydroxide. The potash bulb, *E*, and the two calcium chloride tubes, *d*₁ and *d*₂, are weighed as a unit, and should be designed accordingly. The final tube, *F*, is also filled with 12-mesh calcium chloride.

The initial potash bulb, *A*, is filled with the same strength potash solution as that in *E*. Bulb *A* is connected to balloon flask *B* by means of a side arm sealed into the side of *B*, the inner projection of the arm extending to within 0.5 cm. of the bottom of flask *B*.

The connections between *A* and *B*, and between *R* and *C*, should be made with about 6 inches (15 cm.) of high-grade, thick-walled rubber tubing. This will allow the condenser and flask *B* to be moved up and down.

This apparatus, assembled on a single ring stand, is a permanent set-up. It has been in use in this laboratory for several months and has given satisfactory service. The rubber connections should be changed occasionally.

PROCEDURE. It is assumed that the analyst has some idea as to the amount of carbon in solution. A quantity of the carbon-containing solution sufficient to liberate between 100 and 200 mg. of carbon dioxide is placed in flask *B*. Carbon-free water is added to make a total of about 180 cc. From 5 to 10 grams of powdered potassium persulfate (depending on the amount of carbon and hydrogen to be oxidized) are added, and the flask is rotated to dissolve as much of the reagent as possible. From 5 to 10 cc. of 4 per cent silver nitrate solution are then added, and the apparatus is properly connected. No oxidation occurs in the cold, and it is good practice to pass air through the apparatus for a few minutes to remove the carbon dioxide. Bulb *E*, with its calcium chloride tubes *d*₁ and *d*₂, is then detached, carefully wiped dry, and weighed. The static charge generated on the tube by friction of the towel should be discharged by grounding.

After again connecting the potash bulb to the train, oxidation flask *B* is immersed in water at a temperature of 70° to 80° C. No air is passed through at this time.

As the solution in *B* becomes warm, a black deposit of silver peroxide forms, and at about 70° C. a lively evolution of oxygen gas commences.

The reaction should be maintained at 70° C. until the solution clears up and the evolution of gas has stopped. Usually 15 to 25 minutes are required. Flask *B* is now removed from the water bath and the contents brought to a gentle boil. Air is started through the apparatus at the rate of about 5 bubbles per second. The boiling and aëration are continued for 15 minutes. During the oxidation, the rate of evolution of the gas can be controlled by the temperature, and should not be allowed to exceed 3 or 4 bubbles per second, as there is danger of incomplete oxidation if the oxidant is decomposed too

rapidly. Potash bulb *E* is then removed and weighed with the usual precautions.

If chlorides or combined chlorine is present, enough silver nitrate is added to give about 0.2 gram excess over that required to precipitate the chlorine.

It can be seen from the equation $K_2S_2O_8 + H_2O \longrightarrow 2KHSO_4 + O$, that the solution becomes acid during the process, and consequently there is no difficulty in driving all the carbon dioxide out of the solution. In the presence of silver nitrate the reaction follows a different path, but the end products are the same.

DISCUSSION AND EXPERIMENTAL RESULTS

In view of the objections raised by Cain (2) and others against the gravimetric method for the determination of carbon dioxide, it seems desirable to offer a few remarks in defense of its use under the present circumstances, at the same time admitting its limitations.

In Table I are shown results from a series of blank tests which indicate the errors to be expected due to gain or loss of moisture by the potash bulb. The length of time during which air was passed through the apparatus is indicated in each experiment. In each case the time exceeded that of an actual experiment. The water in flask *B* was kept at boiling temperature, but no reagents were present. Table II shows the results of blanks run on the reagents and water.

TABLE I. BLANKS OBTAINED BY PASSING AIR THROUGH APPARATUS

TIME Min.	GAIN IN WEIGHT Mg.
30	0.0
45	0.2
45	0.5
60	-0.3
60	0.0
120	0.0
120	0.5

TABLE II. BLANK DETERMINATIONS MADE ON REAGENTS^a

$K_2S_2O_8$ Grams	GAIN IN WT. OF POTASH BULB Mg.
5.0	0.4
5.0	0.5
7.5	1.5
7.5	1.0
10.0	0.7
10.0	2.0

^a 0.2 gram of silver nitrate present in 180 cc. of water in each case.

From Tables I and II it can be seen that an error of 2.5 mg. may be expected. This error becomes serious in cases where less than 50 mg. of carbon dioxide are evolved and, in some cases, even where 100 mg. of carbon dioxide are obtained. When the aim is to check the carbon balance in fermentation processes, and when as much as 150 mg. of carbon dioxide can easily be obtained, the accuracy is sufficient. The time required for detaching the potash bulb and weighing it for each experiment is short.

The carbon dioxide-absorbing efficiency of Bowen potash bulbs when filled with 65 per cent potassium hydroxide is perfectly satisfactory. Table III shows results on pure sodium bicarbonate and sulfuric acid. The rate of bubbling air through the apparatus is indicated in the first column. Dilute potash solutions are to be strictly avoided.

TABLE III. EFFICIENCY OF ABSORPTION OF CARBON DIOXIDE^a

BUBBLES PER SECOND	CO ₂ CALCD. Gram	CO ₂ FOUND Gram
1	0.0880	0.0875
2	0.0880	0.0880
5	0.0880	0.0882
5 to 10	0.0880	0.0877

^a 200 grams of 0.1 M sodium bicarbonate present in each case.

Oxidation flasks of less than 200 cc. should not be used. The solubility of potassium persulfate is approximately 5

grams per 100 cc. of water. If the reagent is not in solution, the liberation of nascent oxygen occurs at the solid surface and the oxidizing efficiency is low.

TABLE IV. RESULTS OF ANALYSES

SUBSTANCE	CO ₂ CALCD.	CO ₂ FOUND	RECOVERY
	Mg.	Mg.	%
Acetic acid	176	175	99.4
Propionic acid	132	130	98.5
Butyric acid	176	173	98.3
Chloroacetic acid ^a	88	83	94.3
Thiourea	44	43	97.7
Ethyl alcohol	150	150	100
Succinic acid	176	173	98.3
Dextrose	150	150	100
Dextrose + NH ₄ Cl	100	99	99.0

^a Eastman's c. p. chloroacetic acid used; could not be further purified.

The results of analyses made on solutions containing representative compounds obtained by fermentation of carbo-

hydrates are shown (chloroacetic acid and thiourea are also included in Table IV). From Table IV it can be seen that the presence of sulfur, nitrogen, and chlorine has no serious effect.

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Sulfur Content of Foods

Modification of Turbidimeter for Determination of Small Quantities of Sulfur

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THE necessity for an accurate knowledge of the mineral constituents of our common foodstuffs has increased in recent years. So far as the present authors have been able to find, the data on the sulfur content of foods are fragmentary and are based on different methods of analysis. Sherman (5) has compiled a table listing the sulfur content of many foods. The data are gathered from various sources and the methods used are undoubtedly varied. It is the purpose of this paper to describe a modification of the sulfur turbidimeter adapted to the determination of small quantities of sulfur in foods and biological material following oxidation of the sample with nitric and perchloric acids according to the method of Toepfer and Boutwell (6), and to give the sulfur content of a number of our common foods as determined by this method.

The earlier work (1, 6) from this laboratory was carried out with the old model of the sulfur photometer. The present authors have used a modification of the new model of the Burgess-Parr turbidimeter. The new instrument offers advantages over the old in simplicity, accuracy, and speed, but it requires from 4 to 6.5 mg. of sulfur in a volume of 200 cc. in order to obtain suitable readings. In the case of materials low in sulfur, this would often require too large a sample for oxidation. The authors have modified the instrument so as to make it suitable for use with a working

volume of 25 cc. containing from 0.7 to 1.3 mg. of sulfur. This modification was accomplished by using black hard rubber tubing of a smaller diameter in place of the larger tubes furnished with the instrument as described by Parr and Staley (3). The stationary tube *C*, in Figure 1 in their description, is replaced by a hard rubber tube of 13 mm. inside diameter with an optical glass bottom immediately above the light *L*. This tube holds the turbid solution to be examined and is suitable for use with a volume of 20 to 25 cc. The inner plunger tube, *P*, is replaced by a smaller hard rubber tube of 8 mm. outside diameter, also fitted with an optical glass bottom. The small diameter of the plunger tube gives a small field for comparison but adds to the sharpness of the end point. Suitable metal collars are used to hold the smaller tubes in place in the instrument. This modification is of especial value for work on materials low in sulfur. It has made possible an accurate determination of sulfur in a sample one-sixth to one-seventh as large as would have been necessary if the original instrument had been used. This modification is recommended for the turbidimetric determination of sulfur in urine (1).

The accuracy of the results secured with the modified turbidimeter is shown by the ability to reproduce the calibration curve of the instrument between the optimum range of 0.7 to 1.3 mg. of sulfur with an average error of about

TABLE I. RESULTS ILLUSTRATING USE OF MODIFIED TURBIDIMETER

Wt. of sample, grams Volume (made up to), cc. Aliquot taken, cc. Turbidimeter reading	SULFUR 1 0.3163 500 20			SULFUR 2 0.5565 200 7			SULFUR 3 0.5060 250 14			RED RADISHES 25.81 100 15			APPLE 82.5 50 10		
	I	II	III	I	II	III	I	II		I	II	III	I	II	III
	86	84	84	67	67	67	64	65		67	69	67	61	60	61
	87	84	83	64	65	67	64	63		64	69	68	61	61	60
	85	83	85	65	67	71	63	65		66	69	67	61	62	62
	85	84	84	65	67	68	65	65		65	69	68	60	60	61
	85	82		65	67	68				65			64		
				64		68							61		
Mean	85.6	83.4	84.6	65	66.8	68.1	64	64.9		65.3	69	67.5	61.3	60.9	61
Average		84.5			66.6			64.5			67.3			61.07	
Sulfur found, grams		0.00078			0.00095			0.00099			0.00097			0.00101	
Sulfur present, grams		0.000783			0.000945			0.00099							
Error, grams		-0.000003			+0.000005			0.00000							
Sulfur found, %		6.165			4.93			3.53			0.025			0.012	
Sulfur present, %		6.188			4.84			3.53							
Error, %		0.32			1.6			0.00							

1 to 2 per cent. This represents the limit of accuracy in reading the instrument and applies in any determination. The earlier papers (1, 6) from this laboratory show the ability to recover added sulfur by this method and a comparison of the turbidimetric results with those obtained by the standard gravimetric methods.

TABLE II. SULFUR CONTENT OF FOODS

MATERIAL	SULFUR %	MATERIAL	SULFUR %
Apple (crab)	0.018	Meat (cont'd)	
Apple (Rome beauty)	0.012	Ham (pig)	0.130
Asparagus	0.065	Heart (pig)	0.125
Banana	0.013	Kidney (pig)	0.155
Barley	0.137		
		Lamb chop	0.174
Beans (lima, dry)	0.187	Pork liver	0.266
Beans (navy, dry)	0.250	Pork loin	0.242
Beans (shell)	0.070	Steak (round)	0.202
Beans (soy, dry)	0.290	Shoulder (pork)	0.174
Beans (string, yellow)	0.017	Veal chop	0.069
Beets (red)	0.017	Milk (condensed)	0.126
Beets (sugar)	0.015	Milk (whole)	0.028
Bread (bran)	0.011	Molasses	0.032
Bread (white)	0.011	Muskmelon	0.031
Bread (whole wheat)	0.104	Mustard seed	1.175
Cantaloupe	0.031	Nut meats (hickory)	0.166
Cabbage	0.046	Nut meats (English walnut)	0.135
Carrot	0.016	Oats	0.160
Cauliflower	0.056	Oatmeal	0.233
Celery	0.025	Orange (California)	0.014
Cheese (American Kraft)	0.198	Parsnip	0.036
Cherries (maraschino)	0.041	Peach	0.005
Chocolate (bitter)	0.196	Peanut	0.208
Cocoa	0.236	Pear	0.016
Coffee (bean)	0.131	Peas (dried)	0.154
Corn (yellow, maize)	0.120	Peas (green)	0.031
Corn (sweet, dried)	0.131	Plums (purple)	0.004
Corn (sweet, green)	0.051	Plums (red)	0.005
Corn (gluten)	0.607	Potato (early Ohio)	0.049
Cornflakes	0.114	Potato (sweet)	0.017
Cracker (white)	0.094	Prunes	0.022
Cucumber	0.009	Pumpkin	0.018
Egg (total)	0.167	Pepper	0.035
Egg (yolk)	0.108	Radish (white)	0.019
Egg (white)	0.169	Radish (red)	0.025
Egg plant	0.036	Raisins (seedless)	0.046
Garlic	0.506	Rice (white)	0.136
Grapes (with skins)	0.012	Shredded Wheat	0.164
Hemp seed	0.291	Spinach	0.030
Honey	0.004	Spinach (New Zealand)	0.045
Horse radish	0.221	Squash (Table Queen)	0.029
Jelly (grape)	0.006	Squash (summer)	0.053
Kohlrabi	0.036	Sirup (Karo)	0.029
Lettuce (southern)	0.013	Tapioca	0.012
Lettuce (northern)	0.016	Tea	0.217
Macaroni	0.143		
Meat		Tomato	0.017
Calves' liver	0.225	Wheat	0.145
Brain (pig)	0.113	Wheat flour (40% gluten)	0.470

TREATMENT OF SAMPLE

It is desirable to have sufficient sulfur in the oxidized sample to make possible check determinations. In the course of this work three sets of readings were taken on each sample, so it was necessary to have from 3 to 5 mg. of sulfur in each sample oxidized. The samples used varied in weight from 0.5 gram for materials high in sulfur to 120 grams for materials such as honey which contain little sulfur. The per cent of sulfur in all cases is reported on the wet basis or on the condition in which the sample was offered in the market for food consumption. This was done in order to obtain a more representative sample of the material. It is difficult in many cases to dry a sample of food high in moisture and then obtain a satisfactory sample for analysis. Volatile compounds other than water may be lost at the temperature of the drying oven or even at low temperatures. Peterson (4) has shown a 10 to 20 per cent loss of the volatile sulfur in rutabagas and cabbage on drying the green material in the oven. The figures presented in this paper do not represent the sulfur content of these foods in general, but only the sulfur content of the particular sample analyzed. Only when a large number of samples grown in different

localities and under different conditions have been analyzed will it be possible to state the average sulfur content of any foodstuff.

OXIDATION OF SAMPLE

The method of oxidation was essentially that described in an earlier paper (6). The sample was weighed in its natural condition and was introduced into an 800-cc. Pyrex Kjeldahl flask and digested on the steam bath with 50 cc. of concentrated nitric acid until solution took place. The flask was then transferred to a digestion rack and boiled very gently until the evolution of nitrogen dioxide ceased. If violent bumping occurred, 15 cc. of fuming nitric acid were added. As a rule, this caused sufficient oxidation to prevent further bumping. After the evolution of nitrogen dioxide had stopped, the solution was boiled until nearly all the nitric acid had been distilled off. Then 10 cc. of 70 per cent perchloric acid were added and the boiling continued until approximately one cc. of solution was left. In some cases further treatment with perchloric acid was required. The oxidation up to this point requires from 4 to 6 hours depending on the type of material and the size of the sample. The excess of nitric and perchloric acids was destroyed by adding 10 cc. of concentrated hydrochloric acid and again evaporating to near dryness. The remaining acid was neutralized by adding dilute ammonium hydroxide and boiling to remove the excess of ammonia. The solution was made slightly acid with hydrochloric acid and filtered into a 50-cc. volumetric flask. The correct hydrogen-ion concentration for the subsequent precipitation of barium sulfate was obtained by making the solution alkaline with ammonium hydroxide and then just acid to litmus with hydrochloric acid. The solution was then made up to volume.

A blank determination was made for the sulfur present in the reagents used by running a determination on a solution containing 5 mg. of sulfur. This correction averaged 0.00006 mg. of sulfur.

USE OF MODIFIED TURBIDIMETER

The turbidimeter readings using the modified instrument were obtained by running a suitable aliquot of the solution prepared as above into a 25-cc. volumetric flask. Three cubic centimeters of a solution containing 240 grams of sodium chloride and 15 cc. of concentrated hydrochloric acid per liter were added and the whole diluted to 25 cc. The solution was transferred to a 50-cc. Erlenmeyer flask, 0.1 gram of solid sized barium chloride added, and the solution shaken for about one minute. Turbidimetric readings were taken within the following 5 minutes as described in the bulletin (2) furnished with the instrument. Practice in reading the instrument is essential and frequent checking of the calibration curve is recommended. The instrument should be calibrated by each operator. In the determination of sulfur in urine this same procedure should be substituted for that previously described (1) if the modified turbidimeter is used.

Results illustrating the use of the modified turbidimeter are given in Table I. The data in the "sulfur found" column were obtained from the calibration curve of the instrument. The figures given under the "sulfur" heads represent data on analyzed samples of known sulfate content. No oxidation was involved in their analysis. In no case did the operator know the sulfate content of these samples until after the analysis was complete.

In Table II the sulfur content of ninety-six foodstuffs is given. The results in both Tables I and II are corrected for the blank determination.

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Comparative Efficiencies of Gas-Washing Bottles

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DECISION as to the efficiency of various types of gas-washing bottles is an apparently simple matter, but one which proves quite complex on thorough investigation. Friedrichs (2), in 1919, showed that of the various devices known at that date, only the gas washers built on the spiral-pattern principle could insure complete absorption. Since that time, apparatus with sintered-glass filter disks have been developed. In a paper by Sieverts and Halberstadt (5) it was shown that besides the length of passage in which gas and liquid are in contact with each other, the size of the gas bubbles distributed within the liquid is also of decided importance. These results are referred to in a recent paper by Friedrichs (3). He employed mixtures of sulfur trioxide and air, both wet and dry, and tested the absorption with eleven different patterns of gas washers.

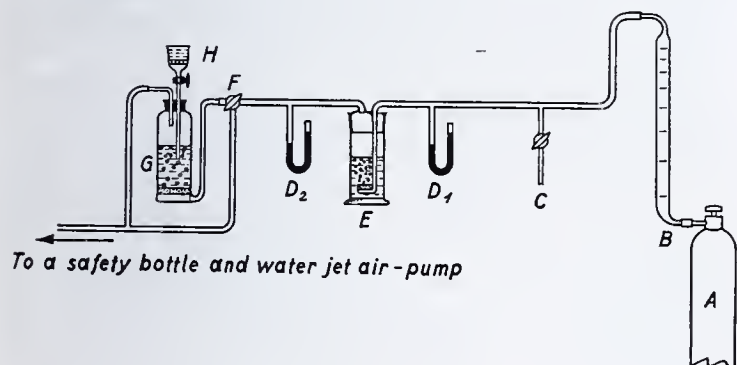


FIGURE 1. MODIFIED APPARATUS

Unfortunately these experiments cannot be compared with former ones because it is well known that wet sulfur trioxide is likely to form a nebula in air and that these nebulas behave quite differently from real gases. It is difficult to absorb them in liquids, but easy to retain them by the action of filters. This is clearly shown by Friedrichs' results. When using a moist mixture of air and sulfur trioxide, a glass-filter gas washer and a spiral gas washer filled with glass grains are most efficient, and have approximately the same effect. When using the dry mixture, the spiral gas washer filled with glass grains gives the same efficiency, owing to the considerable thickness of the filtering layer. On the other hand, the glass-filter gas washers of Schott and Gen. are less efficient because the nebulas are produced only in the thin filter disk in which the gas comes into contact with the liquid, but they are still capable of comparison with the best apparatus without glass filters.

Rhodes and Rakestraw (4), who also studied these problems, came to the conclusion that the spiral gas washers of Greiner and Friedrichs and the pattern 101 of Schott and

Gen. (apparently G1 porosity) gave about the same good results. They employed air containing 13.4 and 5.1 per cent of carbon dioxide, with velocities of flow up to 16 cc. per second—i. e., about 60 liters per hour. They mention that for the glass-filter gas washers, a comparatively higher pressure must be used.

The following experiments were made in accordance with the last-mentioned paper. The gas mixture, contained in a steel cylinder, A (Figure 1), was passed through a flowmeter (Rotameter), then through a gas washer, E, filled with a solution of potassium hydroxide (1 to 2), and through a three-way stopcock, F, to a glass-filter gas washer, 101 G3, containing a clear solution of barium hydroxide, G. The outlet from this led to a water-jet pump. On either side of the gas washer being tested there was placed a mercury manometer D₁, D₂. The differences in height between these two manometers are given in Table I as "resistance of the gas washer."

The gas washer containing the solution of barium hydroxide was constructed in the following manner: The usual ground-glass stopper was replaced by a double-bore rubber stopper carrying an outlet delivery tube and a glass-filter dropping funnel, H. With the three-way stopcock, F, closed, clear filtered barium hydroxide could be drawn into the bottle from this funnel. After every experiment, the filter and the gas-washing bottle were cleaned with hydrochloric acid and carefully washed with distilled water. Then a fresh portion of 75 cc. of barium hydroxide was introduced in the same manner.

The results of these experiments are shown in Table I.

TABLE I. RESULTS OF EXPERIMENTS WITH DIFFERENT TYPES OF APPARATUS

TYPE	HT. OF LIQUID COLUMN Mm.	AV. RESISTANCE OF GAS WASHER Mm. Hg	VELOCITY GIVING REACTION WITH Ba(OH) ₂ WITHIN 5 MIN. 17% CO ₂ 3% CO ₂ 0.67% CO ₂		
			L./hr.	L./hr.	L./hr.
Drechsel	65 95	10	20 20	20 20	20 20
Greiner and Friedrichs	(200 cc. KOH) length of way about 880 mm.	10	60	60	60
Schott 83 G1	65 95	20	30 30	45 45	45 60
Schott 101a G1	40 65 95 140	25	30 45 60 60	45 45 60 75	45 75 75 80
Schott 101 G3	40 60	90	60 75	75 90	100 100

From these data it may be concluded that the Greiner and Friedrichs gas-washing bottle, as also found by Rhodes and Rakestraw, is useful for very many purposes. In certain cases, however, the glass-filter gas washers proved to be superior, since with this type the lower the concentration of the gaseous component to be absorbed, the greater

the permissible velocity. The spiral gas washer can, in all cases, be employed only up to a certain maximum velocity (60 liters per hour) independent of the gas concentration. A possible relationship might be found if the height of the liquid in the spiral washer were varied; in this case, a shorter length of the liquid column should suffice for a more dilute gas. Now with increased flow velocity, the resistances of the gas washers become of less importance. When using finer glass filters (G3), a type which was not available to Rhodes and Rakestraw, this effect becomes even more apparent.

In this connection, it is worth calling to attention a paper by Brückner (1), who made use of a gas washer, pattern 101a, with a glass filter G1, for the determination of minimal concentrations of ammonia in illuminating gas. As compared with previous experiments with older types of gas washers, he could increase the flow velocity up to sixty times the previous quantity (1500 liters per hour).

The filling of the spiral gas washer of Greiner and Friedrichs

with glass grains, after the example of Friedrichs, proved to be impossible in the model used, because in this case the gas passed through the filter from top to bottom, and at high velocity the glass grains were blown out of the interior chamber.

ACKNOWLEDGMENT

The author wishes to thank the Janaer Glaswerk Schott and Gen. for kindly placing at his disposal the necessary apparatus and the steel cylinders containing the gas mixtures that were used.

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Rapid Determination of Small Amounts of Magnesium in Presence of Phosphates

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THE most commonly used micromethod for determining magnesium in biological fluids or ash consists in precipitating the magnesium as magnesium ammonium phosphate from the filtrate of a calcium determination and determining the phosphorus colorimetrically (2, 5).

Bečka (1) described a method based upon the formation of a lake by magnesium with Titan yellow. The method presented here does not require the time needed to perform a determination by the first method nor as many preparations as the second. It is suitable especially for laboratories in which such magnesium determinations are not a routine matter.

The determination is based upon the formation of a lake by magnesium with curcumin (3) in the presence of sodium hydroxide, and its colorimetric comparison with standards prepared simultaneously. The phosphates affect the color of the lake suspension but, if the standard solution also contains dissolved tricalcium phosphate, the color intensities are comparable and in proportion to the amount of magnesium present. Variations in the relatively large amounts of calcium phosphate added in no way affect the color intensities of the standard solution. This fact and a difference in color shade suggests the formation of a magnesium-curcumin-phosphate lake. The lake suspensions may be made more stable by the addition of starch glycerite solution (4). The removal of iron if present in too large quantities is also provided for.

PROCEDURE. Pipet an aliquot of the ash solution (containing about 2 cc. of concentrated nitric or hydrochloric acid per liter) which is equivalent to 0.02 to 0.04 mg. of magnesium into a 50-cc. Nessler tube or volumetric flask. Dilute to about 40 cc., and add 2 cc. of starch glycerite solution (prepared by shaking some of the jelly with water and filtering) and 4 drops of a 1 per cent alcoholic solution of curcumin. Since it is important that the unknown and standard solutions receive the same amount of curcumin, this should be added with a pipet made for the purpose from a capillary tube. Mix contents thoroughly and add 5 cc. of 4 *N* sodium hydroxide. Mix again, dilute to mark, and mix.

One or several standard solutions are treated simultaneously in the same way. A standard solution containing 0.02 mg. of magnesium per cc. is prepared by dissolving 0.203 gram of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.1 to 0.4 gram of tricalcium phosphate in water containing 2 cc. of concentrated nitric acid and diluting to one liter.

In Nessler tubes distinct color intensities are distinguishable with differences of 0.01 mg. of magnesium. The color intensity is, however, less than is desirable for an instrument which allows for a depth of only 5 cm. The Nessler tubes may be used as colorimeters by varying the depth of liquid in them. The solutions are diluted so highly in order to prevent the rapid formation of a tricalcium phosphate precipitate. The lake suspensions are stable for several hours. When viewed through the Nessler tubes the suspensions appear to be slightly cloudy.

If iron is present in sufficient quantity so that an appreciable colored suspension is formed upon adding the sodium hydroxide and diluting, it may be removed as follows: Titrate a separate aliquot with dilute sodium hydroxide to the neutral point of methyl red (pH 4 to 5). Add the same amount of sodium hydroxide to the aliquot to be used and filter or centrifuge out the precipitate. At that pH, the magnesium phosphate is still soluble.

When borates are present in excess of 0.6 mg. (as the oxide) magnesium-free blanks are affected slightly. The color intensities of blanks varying in boric oxide concentration from 1.4 to 8 mg. were the same. Two lake solutions were made up according to the directions given above containing 0.03 mg. of magnesium and 0.6 mg. of tricalcium phosphate. One of them contained in addition 6 mg. of boric oxide. The color intensities of both solutions were apparently the same. The slight effect, if any, of borates when present in larger amounts than 0.6 mg. can be eliminated in two ways. A solution containing 2 mg. of boric oxide may be added to each of the standard aliquots, or the sample aliquot may be evaporated to dryness with hydrochloric acid and methyl alcohol to remove the boric acid and the residue taken up with a

little hydrochloric acid and water and transferred to the reaction vessel.

By this method a synthetic milk ash solution calculated to contain 0.54 mg. of magnesium was found by taking seven colorimeter readings in comparison with a standard containing 0.45 mg. of magnesium to contain 0.52 mg. A partially ashed food composite has 0.40 per cent of magnesium by this method and 0.42 per cent by the modified method of Denis (2).

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The Baro-Buret

III. Application to Gas Density Determinations

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GAS density determinations are of prime importance in the determination of molecular weights for the establishment of new gaseous compounds, the analysis of gaseous mixtures, the study of diffusion and viscosity, and in many other investigations. A rapid, yet accurate, method for the easy determination of gas densities from small samples would be of value.

Early gas density determinations were unsuccessful owing to the lack of suitable containers, pumps, and the means for accurately measuring volume, pressure, and temperature. With the introduction of gas balloons and the modern vacuum pumps, rapid strides have been made in the "balloon" methods of density determination. Morley (16), Rayleigh (18), and Germann (6) undoubtedly made some of the most valuable modern contributions to this method. They used balloons of more than a liter capacity, although some more recent investigators have used smaller ones. All balloon methods, however, are tedious, and present numerous difficulties because of contraction of the balloons on exhaustion and the need of weighing globes and counterpoises. Large samples are required which are slow to reach equilibrium. Corrections are numerous and measurements at pressures greater than atmospheric are impossible because of the fragility of the balloons.

Of other methods for determining gas densities by buoyancy (5, 12), by balancing a column of gas against a column of air (1), or by dynamic methods (9, 13), it may be said that in general large volumes of the gas are required, cumbersome manipulatory details are involved, and the results are not entirely satisfactory.

Volumeter methods (11, 15), in which the volume of a known weight of gas is determined, generally require large samples and give difficulty in the measurement of pressure, volume, and temperature.

Measurements of gases in balloons, followed by adsorption or condensation in small weighing tubes, have been made by several workers (7, 8, 17) of which the recent work of Maass and Russell (14) probably provides

the most accurate simple method. Errors and corrections due to weighing a large balloon were eliminated by first measuring the gas in a balloon, and then condensing it in a small glass ampoule which was sealed off and weighed. The tube was reopened to allow volatilization of the gas and then reweighed. Although a simple U-manometer was used to measure pressure, an accuracy of 0.05 per cent is claimed with the possibility of 0.01 per cent accuracy using a cathetometer. By modifying this method, the pressure, volume, and temperature of a much smaller sample may be measured in the baro-buret and the weight of the sample determined by adsorption and weighing in a glass tube filled with charcoal, as indicated in Figure 1. The use of the baro-buret in gas evolution methods has previously been described (3).

BARO-BURET METHOD

ADVANTAGES. The baro-buret is a simple instrument with the following distinct advantages:

1. It is rapid and easy to use.
2. It requires only a small sample.
3. It may be adjusted to give optimum conditions of volume and pressure (2).
4. It is possible to make several readings on the same sample.
5. It requires few corrections.
6. It is accurate.

The one disadvantage is that the determinations are made at room temperature rather than at 0° C.

APPARATUS. To the baro-buret, described in previous articles (2, 3), there are attached by means of capillary tubing, the flat joints *J* and *J'*, the manometer, the storage balloons, and the vacuum pump connections as shown in Figure 1. All stopcocks are hollow-blown and provided with clamps to permit operating under pressure. Tube *T* permits transfer of the condensed gas from the generating unit to the baro-buret, and by using two such transfer tubes at the flat joints, *J* and *J'*, purification of the gas within the apparatus itself may be accomplished by fractionation. The purified gas may

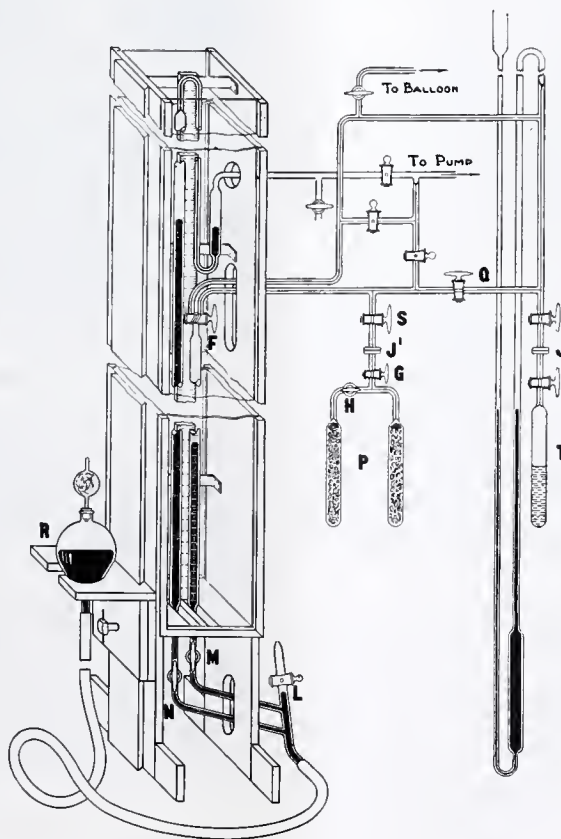


FIGURE 1. BARO-BURET WITH ATTACHMENTS

be taken into the buret from the transfer tube directly, or from the storage balloons. If pressures greater than atmospheric are desired, the gas must be taken directly from tube *T*, since the balloons will not stand a pressure greater than atmospheric. Raising the mercury level in the buret to increase pressure after introduction of the gas is not satisfactory, since some gas "lies down" between the mercury and the walls of the buret and erroneous results are obtained.

The charcoal tube, *P*, is initially prepared by evacuating and then heating to 250° C. in an electric furnace while still connected to the pump. After cooling to room temperature, the tube is wiped carefully with a moist lintless cloth, dried with a silk cloth, and placed in the outer balance case. A counterpoise heavier than the tube itself is similarly moistened, dried, and placed in the balance case. The following day, the tube is weighed and then attached to the apparatus.

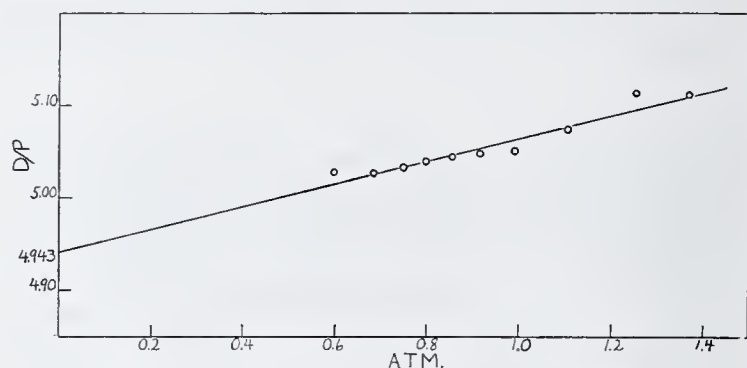


FIGURE 2. LIMITING DENSITY OF CCl_2F_2

OPERATION. With the charcoal tube connected to *J'* as shown, the capillary system and entire buret are evacuated and rinsed several times with small amounts of the gas under observation. If the gas reacts with the stopcock grease, it should be allowed to stand in the system for some time to permit saturation of the lubricant. The system is then evacuated as highly as possible with a good vacuum pump, care being taken to remove gas from both sides of stopcock *F*. Stopcock *Q* is then closed and *F* opened to connect the buret with the balloon or transfer tube.

The gas is permitted to enter the buret slowly to the desired volume at the desired pressure, stopcocks *M* and *N* both being open. The pressure may be controlled by adjusting reservoir *R* previous to the introduction of the gas. Stopcock *F* is then closed and the gas permitted to reach equilibrium with the surroundings (about one-half hour if the room is at reasonably constant temperature). Pressure, temperature, and volume readings are then made (2, 3), and reservoir *R* lowered, if desired, to give a second reading at a different pressure. Stopcocks *M* and *N* are then closed and *F* opened to the charcoal tube, *P*. The arm of the tube bearing stopcock *H* has previously been surrounded with a Dewar flask of liquid air or other refrigerant. Stopcocks *G* and *H* on the charcoal tube are opened. When most of the gas may be assumed to have been adsorbed, stopcock *H* is closed and the remaining gas adsorbed in the other arm of the tube by cooling with the refrigerant.

Complete adsorption was secured in each case, and could be determined by balancing the buret and barometer columns of mercury after opening *M* and *N*, or by evacuating the capillary system and checking the manometer level on opening stopcock *Q*. The mercury is permitted almost to fill the buret. (If gas appears sticking to the walls of the buret, adsorption has been incomplete and the mercury level must be lowered to free the entrapped gas.) Stopcocks *G*, *F*, and *S* are closed, *H* opened, and the charcoal tube set aside to reach room temperature. If *H* is not opened, sufficient pres-

sure may develop to blow out the stopcock plug or break the tube. The charcoal tube and counterpoise are then wiped with a moist lintless cloth, dried with a silk cloth, and allowed to stand in the outer balance case overnight before weighing.

Several runs may be made in the same day by using additional charcoal tubes. Measurement and adsorption require only about an hour or so per tube (two readings), provided the room temperature is reasonably constant. Several charges of the same or different gases may be added one on top of the other in the same charcoal tube. Care should be taken that the gases on warming to room temperature do not develop pressure sufficient to blow out the stopcock plugs or break the tubes.

EXPERIMENTAL WORK. To test the validity and accuracy of the baro-buret for gas density determinations, oxygen was used because at room temperature the gas is far from the critical temperature and corrections for the slight deviation are available. Electrolytic oxygen, kindly furnished by the Ohio Chemical and Manufacturing Company, was further purified by six fractionations with liquid air at pressures between one and two atmospheres. The results are given in Table I.

Two readings of pressure, volume, and temperature were made on samples 3 and 4, with the mean deviations, -0.13 and -0.20 per cent. The observed pressure was multiplied by 1.0016 to correct for the deviation of oxygen (10) and was further corrected for *g*, the gravity constant, and the density of the mercury at the experimental temperature. *Ln* was then calculated by the perfect gas law.

TABLE I. DENSITY DETERMINATION OF OXYGEN

	1	2	3	4	Av.
Wt. of tube before charge, grams	5.14375	9.95142	2.54243	3.78430	
Wt. of tube after charge, grams	5.04099	9.85086	2.40826	3.66921	
Wt. of oxygen, gram	0.10276	0.10056	0.13417	0.11509	
Vol. observed, cc.	96.61	98.40	99.78	98.33	
<i>T</i> observed, abs.	293.91	293.78	295.14	295.49	
<i>p</i> observed, mm. of Hg	613.1	584.6	776.2	676.8	
<i>p</i> cor. to 0° C., atm.	0.8040	0.7666	1.0176	0.8853	
<i>Ln</i> , experimental, grams	1.4215	1.4320	1.4257	1.4248	
Theoretical, grams	1.4279	1.4279	1.4279	1.4279	1.4279
Actual, gram	-0.0064	+0.0041	-0.0022	-0.0031	-0.0019
Deviation, %	-0.44	+0.29	-0.15	-0.22	-0.13

Samples 1 and 2 were weighed on a balance which proved to be insufficiently accurate for this type of work, but the mean of these and several others is fairly close to the theoretical. Samples 3 and 4 check well within the limits of experimental error (discussed later). Since 100 cc. of oxygen weigh only about 0.1 gram, an inexact weight (due to balance, weights, or handling of charcoal tube) introduces a greater error with a light gas like oxygen than with a heavy gas.

TEST ON GAS WITH CRITICAL POINT ABOVE ROOM TEMPERATURE

To test the apparatus further, dichlorodifluoromethane, kindly furnished by the Kinetic Chemicals, Inc., was used after purification in a special fractionating device, to be described shortly in a paper from this laboratory. Results are given in Table II.

In this case, the weighings were probably accurate to 0.03 or 0.04 mg., and the greater weight of sample reduced the error due to weighing. Pressure readings were corrected for *g* and the density of mercury.

Buffington and Gilkey (4), who worked with the same gas, developed the following equation of state:

$$p = RT(V + B)/V^2 - A/V^2$$

where $A = 23.7 (1 - 0.305/V)$
and $B = 0.59 (1 - 0.622/V)$

The units are atmospheres, degrees Centigrade absolute, and liters per gram-mole.

TABLE II. DENSITY DETERMINATIONS OF CCl_2F_2

	1	2	3	4	Av.
Wt. of tube before charge, grams	3.88277	2.49756	9.02133	3.78603	
Wt. of tube after charge, grams	3.37222	1.98644	8.51426	3.28067	
Wt. of CCl_2F_2 , gram	0.51055	0.51112	0.50707	0.50536	
Vol. observed, cc.	99.72	99.94	100.61	99.94	
T observed, abs.	294.82	297.42	297.62	298.02	
p observed, mm. of Hg	763.4	772.0	760.7	764.4	
p cor. to 0°C , atm.	1.0009	1.0117	0.9969	1.0017	
$L_{23^\circ\text{C}}$, atm. (experimental)	5.0932	5.0781	5.0818	5.0811	5.0835
Deviation, actual, gram	+0.0097	-0.0054	-0.0017	-0.0024	+0.0001
From mean, %	+0.20	-0.10	-0.03	-0.05	+0.01

Table III shows the results of calculating the data given in Table II by this equation.

TABLE III. CALCULATION OF DATA BY EQUATION

V	T	p OBSVD.	p CALCD.	$\frac{p(\text{OBSVD.}) - p(\text{CALCD.})}{p(\text{OBSVD.}) \times 100}$
Gram-moles	K	Atm.	Atm.	
23.61	294.82	1.0009	1.0070	-0.6
23.64	297.42	1.0117	1.0145	-0.3
23.99	297.62	0.9969	1.0020	-0.5
23.91	298.02	1.0017	1.0065	-0.5

Thus we find the errors -0.6, -0.3, -0.5, and -0.6 per cent, showing that the values check the equation to about 0.5 per cent, the accuracy claimed by the authors. By this method of calculation, the greatest deviation from the mean is about 0.2 per cent, a value corresponding to that obtained in Table II.

Since the gas is known to deviate greatly and no accurate equation is available, no attempt was made to calculate the weight of a normal liter. Hence the values for the weight of a liter are given at 23°C . and one atmosphere calculated by the perfect gas law, which introduces but a very slight error.

CORRECTIONS AND ERRORS

The observed pressure in any experiment with this apparatus must be multiplied by the correction for g (1.0004 at this laboratory) and by the ratio of the densities of mercury at the experimental temperature and at 0°C . When deviation corrections are known, they should be used as above in the case of oxygen. Errors inherent in the buret and thermometers were eliminated by calibration. The buret was calibrated in place with mercury by means of a stopcock with a fine tip placed just above M . The buret should always be checked in this way, since some burets are made for convex downward menisci, whereas mercury has a convex upward meniscus. The pressure corrections outlined above, together with those for buret and thermometer, are the only corrections required.

In any determination using this apparatus, certain errors are unavoidably present. On the particular baro-buret used, readings of volume could be made to 0.05 cc. on a volume of 100 cc., of pressure to 0.4 mm., of temperature to 0.1°C ., and of weighings to 0.04 mg. on a 0.1-gram sample, giving a maximum error of about 0.20 per cent for a light gas (oxygen) and a somewhat smaller error for a heavier gas. (Additional errors might, however, be introduced if care were not taken in the handling of the charcoal tubes). The errors should be self-compensating and a mean should be very accurate. Individual error could be reduced by using a cathetometer and mirror scale to read pressures and volumes, and an error of not over 0.1 per cent should be easily secured.

DETERMINATION OF LIMITING DENSITY

To determine the possibility of using the baro-buret for determining molecular weights of small samples of gas by

the limiting density method, a set of readings was made between pressures of 0.6 and 1.4 atmospheres. All readings were made on the same sample of gas and the results are shown in Table IV.

TABLE IV. CALCULATION OF LIMITING DENSITY

(Wt. of CCl_2F_2 sample, 0.20879 gram)			
V COR.	$D_{25^\circ\text{C}}$	p COR.	D/p
25°C .	Grams/liter	Atm.	
29.75	7.01815	1.36959	5.12428
32.51	6.42233	1.25195	5.12986
37.25	5.60511	1.10492	5.07287
41.72	5.00455	0.99085	5.05076
45.24	4.61516	0.91440	5.04720
48.43	4.31117	0.85459	5.04472
52.10	4.00749	0.79530	5.03897
56.39	3.70261	0.73567	5.03298
60.76	3.43631	0.68362	5.02664
69.52	3.00331	0.59731	5.02806

Readings of volume were made at temperatures between 25° and 30°C . and corrected to 25°C . by the perfect gas law. Pressures were corrected as in the earlier tables. D is the weight in grams of one liter of the gas at pressure p .

Figure 2 is intended to show that the straight line through the calculated limiting density (4.9433) passes through the average value of the points, rather than to establish the limiting density. The accuracy needed to establish the molecular weights of a gas could be secured by averaging several such determinations.

DISCUSSION AND CONCLUSION

The baro-buret has been shown to provide a rapid and accurate means for the determination of gas densities using a small sample. The apparatus is comparatively easy to build and use. Few corrections are necessary.

When the apparatus is used to determine molecular weights to assist in identifying unknown compounds, the possibility of deviation from the perfect gas law must be kept in mind. By taking readings at several pressures, with each sample the molecular weight can be readily determined by the method of limiting densities (15) and only one set of weighings is required.

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CHEMISTS IN THE BUREAU OF CHEMISTRY AND SOILS have demonstrated that hydrochloric acid and sulfuric acid cause the deterioration of paper. When chlorine compounds are used in bleaching paper pulp, hydrochloric acid may form in the finished product unless the pulp is washed clean. Alum is generally used in sizing paper and if present in excessive quantities will cause deterioration of the finished product. The paper must be virtually free from acid or it will not endure.

Glass and Quartz Filters for Handling Gases

A Review

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GLASS filters for separating solids from liquids have been in use for some years, and a number of American investigators have published researches involving their application since the first notice of them (47) appeared. In the meantime, the wider use of this convenient form of apparatus has been considerably extended by the development of many unique applications, particularly in Germany. Since the researches dealing with these have most largely appeared in German publications, and since the use of filters of this kind in working with gases presents many novel features of special convenience to investigators in this field, it has been thought desirable to review briefly here the progress that has been made along this line. The appended bibliography provides references to methods of applying the new technic in many lines of investigation.

Glass filters are made of ground and sifted glass powder fritted in suitable molds (without any added binder) into porous disks of glass (5, 32) which may be fused into any desired shape of solid glass of the same coefficient of expansion. By selecting the glass used, any desired qualities of chemical or temperature resistance may be had. Ordinary soft glass or special glasses, such as Jena G20 resistance glass, and even fused quartz (27) may be used, and it is possible to use special jointing glasses to permit fusing filter disks to other glasses (such as Pyrex) forming the apparatus where necessary. Many standard forms of apparatus embodying such filters are shown in the accompanying illustrations (courtesy Fish-Schurman Corp., 230 East 45th St., New York, N. Y.).



FIGURE 1.
GLASS FILTER
FOR MERCURY
PURIFICATION

SOME USES OF GLASS AND QUARTZ FILTERS

During the past ten years or so an increasing amount of work has been done with gases in large and complicated vacuum apparatus, and in connection with this several interesting applications of glass filters have been devised. Whereas coarse-grained filters will allow mercury to pass through, retaining dirt, dust, and solid amalgams (Figure 1), fine-grained glass filters will retain mercury even against a pressure of one atmosphere. Making use of this peculiarity, Stock (44, 62) was one of the first to include a glass filter in his apparatus for interrupting gas flow. Stock's device (Figure 2) may be used as a safety valve in a vacuum line by placing a vessel of mercury under the lower stem. A single filter of this kind (Figure 3) may be similarly used as a gas valve by placing a layer of mercury on top of the filter disk, thus allowing gas to pass one way but not the other. Hein (22, 23,

Glass filter apparatus with porous glass filter disks sealed into solid glass walls have been shown to be extremely useful for many laboratory operations where gases are to be treated. These are briefly reviewed here and a copious bibliography refers to many investigations using this technic. Applications discussed include mercury traps, explosion safety valves, dust filters, and gas-liquid reaction vessels. High-velocity gas flow in such apparatus is especially characteristic of glass filter apparatus, and this is important in gas analysis where small quantities of an impurity in large volumes of gas are to be determined, in air-conditioning for textile tests, in flotation experiments, and in physiological and biochemical work.

46, 69) proposed that similar devices (Figure 4) be used as a pressure regulator connected to the top bulb of a Kipp apparatus, especially for generating carbon dioxide in elementary microanalysis after Pregl.

Glass filters may be used advantageously as diffusion membranes, since the diffusion rate of any particular filter is constant and depends upon the porosity as established by the grain size of the glass of which the filter disk is made. Membranes of this kind may form an integral part of gas flow measuring devices (13). Similarly, such membranes have been used by Bennewitz and Neumann (8) for preventing

uneven flow of gas to their catalyst in studies of the impulses in heterogeneous catalysis. Martienssen (18) has utilized this property of glass filters in a device for detecting the presence of an explosive mixture in the air of coal mines by using them as membranes to separate the reaction chamber containing an electrically heated platinum wire from the outer air. The device operates on the same principle as the Davy safety lamp, but is safer since the glass filter cools the flame more thoroughly than a wire gauze and thus prevents its outward passage.

Similarly glass filters fused into glass tubes may be used to advantage as safety valves to prevent gas explosions in laboratory work (49, 50). When an explosive gas mixture is passed through a tube, like that shown in Figure 5, into the small end and is ignited at the wide end, even a coarse filter will prevent the explosion from going beyond it. This

is much more effective than the use of copper gauze, and ordinary glass filters will withstand the temperature of the flame of an explosive mixture of illuminating gas with air. A quartz tube with a quartz filter are necessary on account of the higher temperature if oxygen replaces air. The flame moves from the open end to the filter, and there surface combustion (after Bone) may be seen. Even with the most explosive mixture of hydrogen and oxygen the filter is not damaged, but when a white heat is reached, the gas back of the filter ignites at the hot surface. This apparatus lends itself to the determination of the explosive characteristics of air-petroleum mixtures, among others.

Using this principle, Grote of the Edeleanu G. m. b. H., Berlin, was able to devise a method of making Heslinga's (64) determination of sulfur in liquid fuels easy and convenient.



FIGURE 2. DOUBLE
MERCURY TRAP
AFTER STOCK



FIGURE 3. SINGLE
FILTER
MERCURY
SAFETY
VALVE

The apparatus (10) is shown in Figure 6. The quartz tube is 520 mm. long and is fitted with a diaphragm having an opening 5 mm. in diameter and two coarse quartz filter disks. The sample, in a porcelain dish or open glass ampoule, is placed in the left end of the tube and compressed air or oxygen is supplied. The first filter disk serves as a safety valve to prevent backfire, and the second serves as the combustion surface. The oxidation products, containing carbon dioxide and sulfur dioxide, are conducted through the glass absorption vessel (fitted with a glass filter disk to insure complete absorption) containing a known quantity of hydrogen peroxide, and the sulfuric acid formed is then titrated in the usual way. This method has been used and approved by a number of investigators (56) and seems likely to be adopted as standard in Germany.

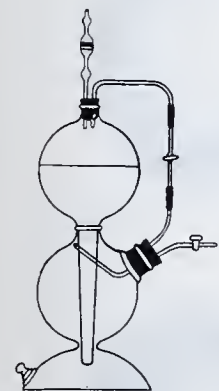


FIGURE 4. KIPP GAS GENERATOR WITH HEIN'S MERCURY SAFETY VALVE ON TOP

Many investigators have used glass filters for separating solids from gases even at elevated temperatures (25, 33, 51, 54, 55), and since different porosities are to be had to meet different conditions, they have proved highly practical for a variety of researches. By proper selection of porosities, high gas velocities can easily be obtained without sacrifice of efficiency. The apparatus shown in Figure 7 has been proposed for the determination of tar in illuminating gas (6, 34), and has been used with considerable success for this purpose. A measured flow of gas passes first over cotton wool to remove coarse droplets, then over a coarse glass filter to remove tar mist, and finally over a finer glass filter to insure complete separation.

An interesting method of analyzing aluminum and its alloys using glass filters has been developed by Jander (29, 30). The apparatus is shown in Figure 8. A stream of dry hydrochloric acid gas coming from the left hand side is passed over the metal shreds in the porcelain boat and thence through a coarse-pored glass filter in front of the glass

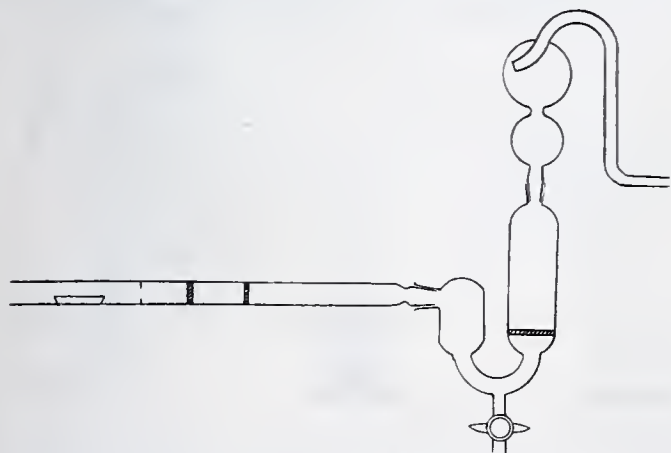


FIGURE 6. APPARATUS FOR DETERMINING SULFUR IN LIQUID FUELS AFTER GROTE

fitting and on to the absorption apparatus. If magnesium is present in the sample, magnesium chloride may be removed from the gases before they reach the filter by applying the Cottrell electrical precipitator principle. This is done by sealing a molybdenum wire into the tube to serve as one electrode, and placing a metal band around it to serve as the other. The

high voltage applied across these electrodes flocculates the magnesium chloride and prevents its passage through the glass filter. Aluminum oxide present in the sample does not combine with the hydrochloric acid under these conditions and may be determined separately from the metallic aluminum which passes the filter as the volatile chloride along with silicon tetrachloride. The temperature of the process may be 200° to 350° C., depending upon the metals present. A simpler apparatus for microanalysis and micropreparations (Figure 9) has been developed by Soltys (60).

In all glass apparatus where reactions are to be carried out between solids and gases, glass filters are very convenient.

Mittasch (43) has used this technic in studying the decomposition of ammonia over metallic iron, and Huettig (26) applied it to the catalytic splitting of methanol by zinc oxide.

One of the most important applications of glass filters is in securing intimate contact between gaseous and liquid phases, a technic principally developed in Germany. In the United States, Edgar and Calingaert (11) used a glass filter tube in determining the sulfur content of gases from combustion of gasoline, and Degering (8) proposed a similar device as an efficient gas-liquid reaction tower.

DETERMINATION OF PORE SIZES AND SIZE OF BUBBLES

In applications of this kind, the value of glass filters depends upon their ability to break the gas stream up into tiny bubbles while allowing it to pass at relatively high velocity.



FIGURE 8. GLASS FILTER TUBE AFTER JANDER FOR ANALYSIS OF ALUMINUM ALLOYS

On this account, a method of estimating pore size and its relation to bubble size in different filters and with different liquids is valuable. Bechhold (1) showed that the pressure drop occurring at a gas-liquid interface is directly proportional to the capillary constant of the liquid and inversely proportional to the pore diameter. His formula was rediscovered by Einstein and Muehsam (12), and measurements of the kind have been widely used for determining maximum and average pore diameters for different filtering materials (24A, 53). A simplified form of the Bechhold equation (48) will serve for practical laboratory use as follows:

$$2r = \frac{4\pi \cdot b \cdot 10^4}{p \cdot 1.033}$$

where $2r$ = diameter of pore emitting bubbles, microns
 b = barometric pressure, mm. of mercury
 π = capillary constant of liquid employed
 p = manometric pressure drop, mm. of mercury
 $1.033 \cdot 10^6$ = pressure of one atmosphere, dynes

Later Bechhold (2) and Schnurmann (54A) showed that this equation is not strictly correct, and that some variation

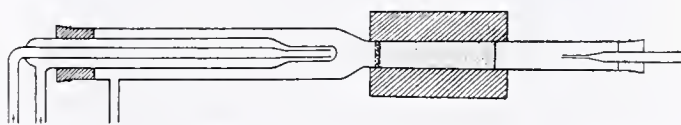


FIGURE 9. SUBLIMATION APPARATUS WITH GLASS FILTER AFTER SOLTYS



FIGURE 7. DOUBLE GLASS FILTER FOR TAR DETERMINATION AFTER BRÜCKNER



FIGURE 5. EXPLOSION SAFETY VALVE

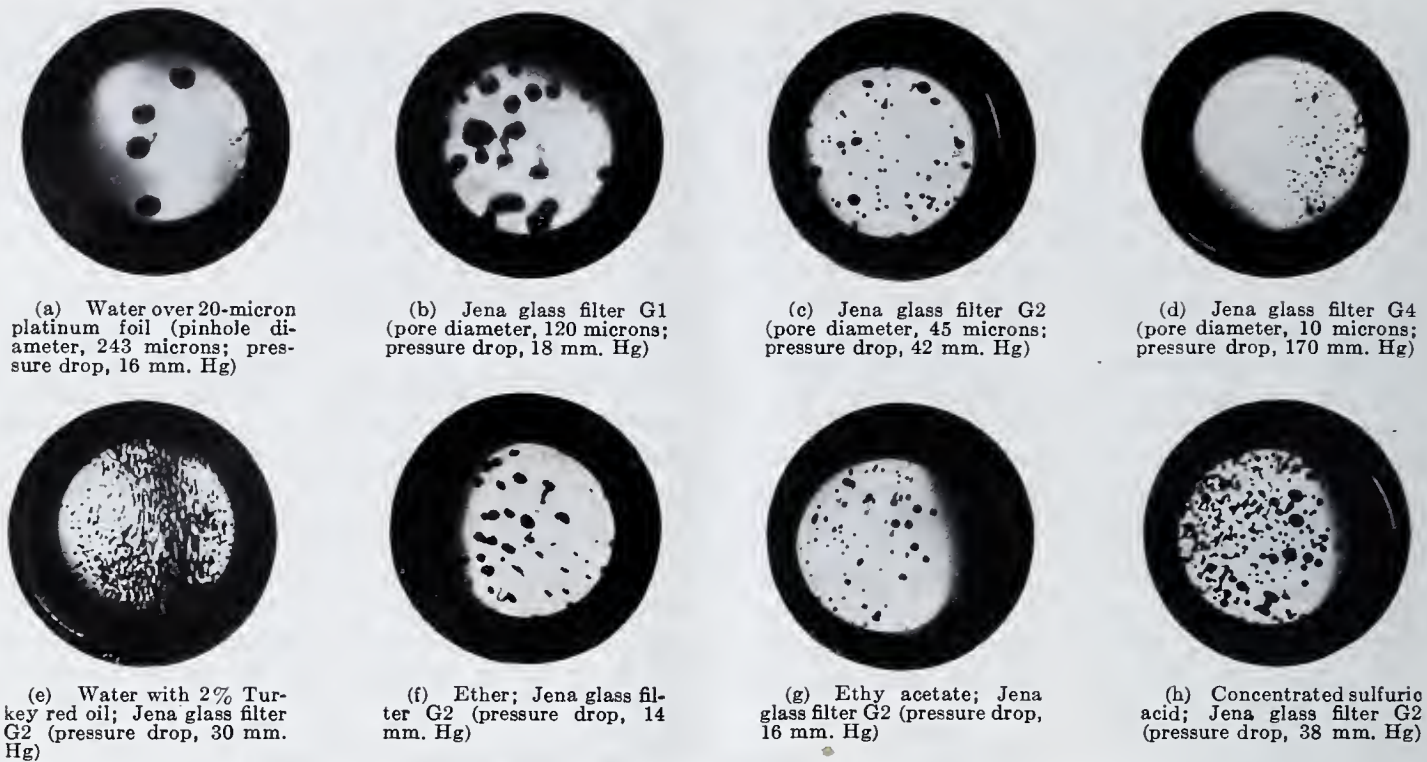


FIGURE 10. PHOTOGRAPHS OF AIR BUBBLES IN LIQUIDS (3/4 NATURAL SIZE)

was found between the values of $2r$ for a porous diaphragm when different liquids are used, as well as with two immiscible liquids brought together across it.

The size of bubbles produced by a porous diaphragm is not the same as the pore size, but is always larger than the capillary diameter (42) and depends on the nature of the liquid used (2, 54A). To take this into account, Halberstadt and Prausnitz (19) have devised a method of studying the bubbles themselves depending upon photographing them as they rise between the parallel walls of a kind of inverted cuvette. This investigation is of sufficient interest to justify rather careful consideration here. Its principal conclusions may be summarized as follows:

Different pore sizes of glass filters require different pressures; the smaller the pores, the higher the pressure. Plotting the gas bubble size against pressure drop for glass filters of different pore diameters yields a hyperbolic curve when either water or ether is used.

There is a distinct optimum of distribution contact between gas and liquid for pore diameters between 14 and 34 microns. A further decrease in pore diameter only slightly decreases the size of gas bubbles, but requires a considerably higher pressure.

Using a glass filter of medium porosity (Jena G2; average pore diameter 34 microns), the size of the gas bubbles formed in different liquids varies widely. The following bubble diameters were measured under these conditions, using the same glass filter:

LIQUID	BUBBLE DIAMETER Microns
Water	490-1240
Ether	270-1650
93.6% alcohol	450-1660
Ethyl acetate	480-740
Carbon tetrachloride	450-800
88.2% glycerol	2330-2890
Sulfuric acid (concentrated)	1060-1330
Water containing 2% Turkey red oil	350-500

Although this series of experiments was not sufficiently extensive to relate the physical constants of the liquids completely to the bubble size, yet it is obvious that the addition

of a surface-active substance like Turkey red oil exerts a profound influence in reducing bubble diameter, and that such additions may therefore be most valuable for increasing the gas surface developed with any specified diaphragm. A coarse filter working with a low pressure drop will form small bubbles where the nature of the reaction desired permits the addition of such materials. Figure 10 shows some of the photographs (three-fourths natural size) of bubbles taken at pressures sufficient to allow the whole filter surface to pass gas, together with a similar photograph for comparison purposes showing the bubbles from a perforated platinum foil.

APPLICATION OF GLASS FILTERS

Glass filters, used for a variety of operations requiring the intimate contact between a gas and a liquid, have been built into many different types of apparatus (Figures 11 to 18, inclusive), and for use in these are available with pore diameters from 1.5 to 250 microns. The most popular pore sizes are 120 and 45 microns. The principles of construction of the various apparatus will be clear from the illustrations.



FIGURE 11. GLASS FILTER GAS-DISTRIBUTING TUBE

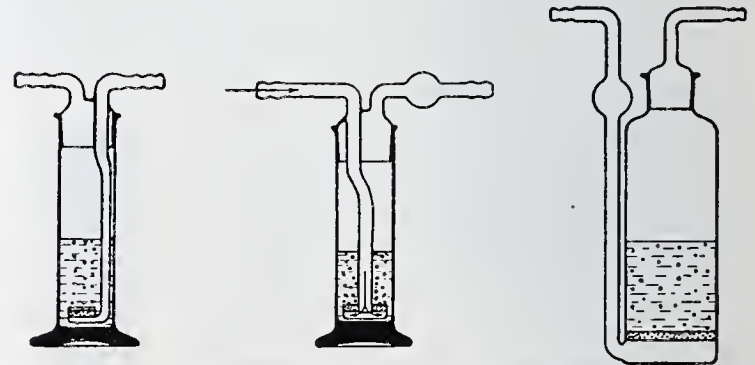


FIGURE 12. SCHOTT-JENA GAS WASHER
FIGURE 13. SCHOTT-JENA GAS WASHER WITH CENTRAL TUBE
FIGURE 14. SCHOTT-JENA GAS WASHER (LARGE TYPE)

The application of these various forms to particular problems has been developed by a number of investigators; Heinrich and Petzold (24) for sulfur determinations; Slotta and Heller (59) for organic hydrogenations; Gehlen (17) for the reaction between nitric oxide and alkaline hydrosulfite;

Sieverts and Halberstadt (58) for oxygen absorption; Vorlaender and Gohdes (66) for nitric oxide absorption; Berl (4) for general gas analysis; Tschopp (65) in microanalysis; Pfyl and Schmitt (45) and Heiduschka (20, 21) in the determination of nicotine in cigarette smoke; Strobl (63) in Orsat apparatus to replace platinum foil proposed by Shepherd

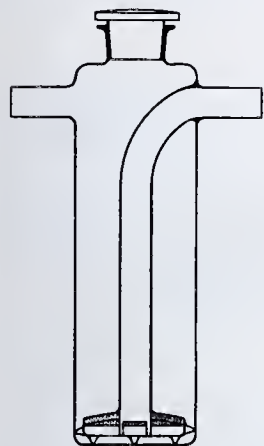


FIGURE 15. LARGE GAS WASHER AFTER KOELLIKER AND DWILLING

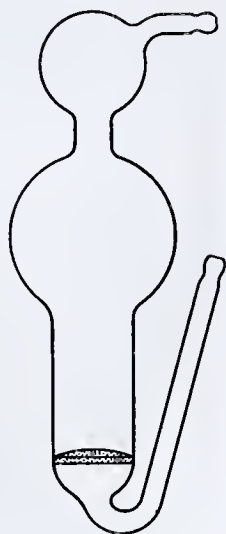


FIGURE 16. GAS WASHER FOR PHYSIOLOGICAL CARBON DIOXIDE DETERMINATION AFTER KNIPPING

(57); Brückner (64) for determining ammonia in illuminating gas; Koelliker (37) for detecting minute traces of impurities in the atmosphere; Loeffler (40) and Dietrich (9), tandem glass filters for determining benzene in air.

The methods used by Brückner (64) and Koelliker (37) are particularly interesting, since by utilizing the efficiency of glass filters at high gas velocities, they have developed a technique for detecting and determining extremely minute traces of impurities. Using a gas-washing bottle as shown in Figures 13 (31), 14, or 15, they draw a large measured volume of gas through the absorbent solution at velocities as great as 50 liters per minute, obtaining excellent results.

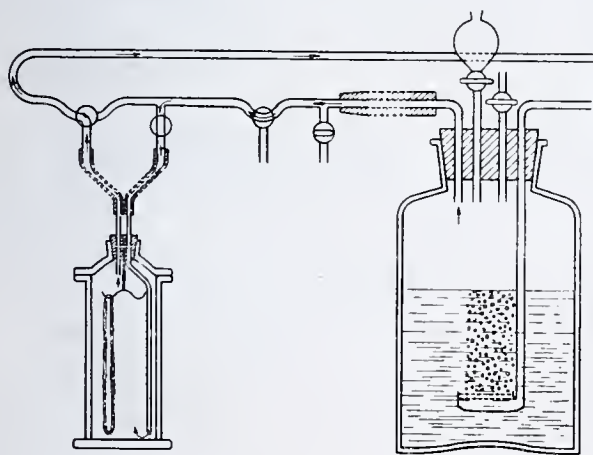


FIGURE 17. AIR-CONDITIONING APPARATUS AFTER WELTZIEN

At low gas velocities the Friedrichs (16) screw type gas scrubber has been shown by Sieverts and Halberstadt (58) to be about equal to a coarse-pore G (Figure 1) glass filter, but these investigators have shown that as velocity is increased or a finer glass filter, G3, used, the latter is more efficient. With glass filters the pressure required to break down the initial film to allow the gas to pass looms large in the total pressure where low velocities are used, as by Friedrichs (15) in sulfur trioxide absorption and by Rhodes and Rakestraw (52) in absorbing carbon dioxide at low velocities. Fischer and Hess (14) also worked at low velocities in absorbing sulfur trioxide. How-

ever, at high velocities Koelliker and Dwilling (personal communication) have shown that the resistance to flow introduced by the narrow tubes and abrupt curves of the Friedrichs apparatus may become as great as that of the glass filter. Using the apparatus shown in Figures 14 and 15 at gas velocities as great as 120 liters per minute, they have found that the pressure drop in the latter type (Figure 15) at this velocity is comparable with that obtained by Rhodes and Rakestraw (52) in the former type (Figure 14) at a velocity of only one liter per minute. Obviously with velocities as great as 120 liters per minute through a filter 60 mm. in diameter available at a pressure of less than 400 mm. of water column, many new possibilities in the treatment of large volumes of gases are available.

Utilizing this high-velocity characteristic Knipping (7, 36) has devised an apparatus for determining carbon dioxide produced by a person during hard labor (Figure 16). An enclosed air volume (with oxygen added as needed) of only 3.2 liters is circulated at a rate of 40 liters per minute to the subject with continuous removal of carbon dioxide. A somewhat similar arrangement for treating an enclosed volume of air to secure continuously a definite humidity for textile tests has been developed by Weltzien (67, 68). In this (Figure 17) air from the enclosed space whose humidity is to be controlled is pumped through aqueous sulfuric acid of a known vapor tension at high velocity.

In bacteriological work, Kluver (35) uses a conical vessel with medium pores, G3 filter (Figure 18), for aerating yeast cultures. Kraeber (38) uses a similar but cylindrical vessel in flotation experiments. Large technical glass filters may be had in diameters up to 610 mm., and these are already finding considerable use in industry for such operations as forcing corrosive gases into solutions (28) and in numerous other operations.



FIGURE 18. YEAST AERATION VESSEL AFTER KLUYVER

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Notes on Systematic Qualitative Analysis of Anions

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ALTHOUGH many qualitative systems of cation analysis have been developed, up to the present time there is no generally accepted scheme for the anions in which each of the various groups is separated consecutively from one sample. It is believed that the following method of group separation makes this possible. The first group removes all those ions which ordinarily interfere with the clean-cut use of the well-known group precipitants in a consecutive system, so that the well-known groups then fall naturally into the remainder of the scheme. There is no overlapping of the groups, inasmuch as each group reagent provides complete separation. A system has been developed (3) which includes thirty-one anions.

One gram of the unknown substance (in solution unless acid-soluble) is neutralized with 6 *N* acetic acid in a stoppered Erlenmeyer flask fitted with a thistle tube and strips of lead acetate, starch-iodide, and potassium chromate papers held by the stopper, and a delivery tube dipping into baryta or lime water. The delivery tube should have a small bulb blown in it to contain slightly moistened potassium permanganate crystals to prevent sulfur dioxide from reaching the baryta water (2). Three milliliters excess acetic acid are added to the solution through the thistle tube and the mixture is heated to 65° C. for one minute, which will liberate hydrogen sulfide, chlorine from hypochlorite, sulfur dioxide from thiosulfate but not from sulfite (unless over 150 mg. of sulfite are present), and carbon dioxide. These gases are detected, if present, by the means provided in the above description. A special thiosulfate test is advisable, and Eastman Formula HT-1 will detect one mg. (1).

Two milliliters of 6 *N* ammonium hydroxide are added through the thistle tube followed by nickel acetate to pre-

cipitate sulfide, if present, completely, and the cyanogen group (cyanide, ferrocyanide, and ferricyanide), which may be filtered off and the individual ions separated according to standard procedure (4). The filtrate is reacidified and boiled to evolve the liberated gases completely. Only a negligible amount of sulfite will be decomposed by this treatment.

The barium group may now be precipitated from the above neutralized filtrate by means of barium acetate, followed by the silver group from slightly acid solution by means of silver acetate, each of these groups to be treated now according to the standard practice of nonconsecutive systems. The soluble ions are detected very easily by common tests, inasmuch as all possible interfering ions have been removed.

In general, at least one to three mg. of each anion can be detected in the presence of 300 mg. or more of other anions. In the first group in the presence of the weak acid there will not be sufficient reaction between sulfide and sulfite to prevent the detection of each at the usual point. This method of group separation makes possible quick and accurate detection of the negative ions.

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Functional Relationship between Ash Content and Electrical Conductance of Cane Sirups and Molasses

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IT HAS been shown in previous papers (1, 7) that the ash content of various kinds of sugar-cane products, such as raw and refined sugars, raw and refinery sirups, and molasses, can be determined by means of conductivity measurements. A specific equation was proposed for each type of product, and in this way the differences among the samples due to their heterogeneous geographical origins, which brought about a variability in the composition of the non-sugar impurities, and their subsequent processing, can be appropriately taken into consideration. The following conductometric formula was developed for determining ash in both raw and refinery sirups and molasses (2) under the condition that 4.5 grams of pure sucrose are added to each 0.5 gram of sugar product before making up to 100 ml. of total volume:

$$\% \text{ ash} = 0.019137 K - 0.002249 K_2 - 0.00121 K_3 + 3.07$$

where K is the specific conductance $\times 10^6$ of the solution prepared as above; K_2 that of a solution made by adding 5 ml. of 0.25 N potassium hydroxide to 200 ml. of the above solution; and K_3 that of a solution made by adding 5 ml. of N orthophosphoric acid to 200 ml. of the above solution.

The sucrose was added for the purpose of preparing a synthetic raw cane sugar solution. In this way it was hoped possibly to relate the analysis of sirups and molasses directly with the method of determining ash conductometrically in raw cane sugars (5, 6).

For routine work, the omission of sucrose from each solution would be advantageous, and so conductometric determinations were made, without the addition of sucrose, on 149 samples of molasses and sirups which had remained in the laboratory from the previous work. Aside from the fact that 0.5 gram of the sample alone was taken for each 100 ml. of solution, no changes were made in the experimental procedure (1-7).

The formula which was found to hold under these conditions is as follows:

$$\% \text{ ash} = 0.01556 K - 0.001125 K_1 - 0.000623 K_2 - 0.000219 K_3 + 3.083$$

The meaning of the various K 's is the same as in the first formula; K_1 represents the specific conductance $\times 10^6$ of the solution obtained by adding 5 ml. of 0.25 N hydrochloric acid to 200 ml. of the solution of the product, as specified above.

The new formula indicates that four conductivity determinations must be made in order to calculate the ash percentage. The reason for this will be explained below. It will be remembered that conductometric ash determinations in raw

An empirical formula has been developed for predicting the ash percentage in cane sirups and molasses from conductance measurements in the presence of hydrochloric acid, phosphoric acid, and potassium hydroxide, but without the addition of sucrose to the sample.

The formula was developed, on the basis of the statistical technic of multiple regression, out of the interrelations existing among the conductance values corresponding to the percentage of chemical ash. The error in the ash percentage calculated by this method is but 3 parts in 93, whereas the permissible error in the chemical method is about 3 parts in 50.

sugars require only two conductance measurements (4). The formula in question was readily derived by simple graphic and arithmetic methods. But when it was later found that in the case of sirups and molasses at least three conductivity determinations are necessary, the derivation of the required formula proved to be a laborious task. It was therefore decided to have recourse to statistical methods, and the cooperation of one of the present writers was invited. The formulas given in the later papers of this series were calculated

by him on the basis of experimental results. The methods by which the formulas were derived will undoubtedly prove of interest, and they are therefore briefly explained here.

Statistical method has developed a numerical measure of the relationship existing between two variables on the assumption of linearity. By linearity is meant that the equation relating one variable to another is of the nature:

$$\begin{aligned} x &= by + c \\ y &= dx + f \end{aligned}$$

where x and y are deviations from the means of the X and Y distributions, respectively.

The multiplying factors, d and b , are known as the "beta weights." The square root of the cross product of the two beta weights is defined by the worker in statistical mathematics as the correlation coefficient. In the case in which a variable is completely a function of another variable, the product of the two betas is equal to one and the correlation coefficient is obviously ± 1 . There are, however, many instances when, owing to lack of precision in measurements or lack of complete functional relationship among variables, a variable is not completely determined by a weighted measure of another. Such deviations from complete prediction give rise to correlation coefficients other than ± 1 . The predictability on the basis of correlations less than one varies approximately as the square root of $1 - r^2$, where r is the correlation coefficient. Whenever complete predictability is impossible upon the basis of the data, we have two equations as above. The b is defined as

$$r_{xy} \frac{\sigma_x}{\sigma_y}$$

where r_{xy} is defined as the correlation coefficient measuring the relationship between variable x and variable y , and σ_x is defined as the square root of the mean of the sum of the squares of the deviations around the mean of the X variable. σ_y , similarly, is defined as the square root of the mean of the sum of the squares of the deviations around the mean of the Y variable. Mathematically,

$$r_{xy} = \frac{\sum xy}{N\sigma_x\sigma_y}$$

where σ_x and σ_y have the same meaning as before, and the $\sum xy$ refers to the cross product of the deviation from the mean of the X variable with the deviation from the mean of the Y variable, summing from sample to sample over all samples, and N refers to the number of cases or population.

When the problem is simply the prediction of one variable from another, the calculation of the single correlation coefficient relating the two and the computation of the sigmas is all that is necessary to the development of a prediction formula, or, as it is known in statistics, a regression equation. The regression equation thus obtained is developed under the assumption that all measurements have the same reliability. By reliability is meant the degree to which confidence can be placed in a single measurement of the variable. For instance, it is assumed in this paper that the average of a duplicate chemical determination of sugar ash is so accurate that any redetermination of the same sugar ash for the same sample will yield the same result. This, obviously, is not true except within certain experimentally and statistically determinable limits. The formula

$$r_{xy} = \frac{\sum xy}{N\sigma_x\sigma_y}$$

makes for a cumbersome computational technic. There are various computational forms which will yield the same result. The formula used for computing the correlation coefficient for this particular paper is

$$\frac{\frac{\sum XY}{N} - \left(\frac{\sum X}{N}\right)\left(\frac{\sum Y}{N}\right)}{\sqrt{\frac{\sum X^2}{N} - \left(\frac{\sum X}{N}\right)^2} \sqrt{\frac{\sum Y^2}{N} - \left(\frac{\sum Y}{N}\right)^2}}$$

where X and Y refer to the actual value of X and of Y , and X^2 and Y^2 to the squares of such values. Then

$$\begin{aligned} \frac{\sum X}{N} &= \text{arithmetic mean of } X \\ \frac{\sum Y}{N} &= \text{arithmetic mean of } Y \end{aligned}$$

$$\begin{aligned} \text{and} \quad \sqrt{\frac{\sum X^2}{N} - \left(\frac{\sum X}{N}\right)^2} &= \sigma_x \\ \text{and} \quad \sqrt{\frac{\sum Y^2}{N} - \left(\frac{\sum Y}{N}\right)^2} &= \sigma_y \end{aligned}$$

For example, our data sheets show for chemical ash and K the following three sample observations:

SAMPLE	CHEMICAL ASH (X)	K (Y)
354	7.31	474.7
355	6.96	443.5
356	6.71	426.2

The sum of such terms as (7.31×474.7) and (6.96×443.5) and (6.71×426.2) will yield $\sum XY$. The sum of such terms as 7.31, 6.96, and 6.71 will yield $\sum X$, and the sum of such terms as 474.7, 443.5, and 426.2 will yield $\sum Y$. The sum of such squares as $(7.31)^2$, $(6.96)^2$, and $(6.71)^2$ will be $\sum X^2$. The $\sum Y^2$ will be the addition of terms like $(474.7)^2$, $(443.5)^2$, and $(426.2)^2$. The manipulation of these terms will yield the needed correlation coefficient.

The above computations, as has been pointed out, are sufficient for obtaining a regression equation predicting one variable from another. When, however, the predictability of one variable from only one other leaves too large a margin of error, it is possible to make use of multiple regression, by which technic the regression equation predicting a criterion variable from a dependent variable is improved by utilizing

the relationships that may exist between the criterion and some other dependent variable or variables.

When the number of variables, including the criterion, is greater than two, the number of correlation coefficients that must be computed to obtain a multiple regression equation is equal to

$$\frac{n(n-1)}{2}$$

where n refers to the total number of variables. In developing the equation reported in this paper, five variables are used: ash (the criterion variable), K , K_1 , K_2 , and K_3 , where the K 's are the conductometric readings as previously defined. Hence, ten correlations must be computed among these five variables. Table I gives the correlation coefficients obtained between ash and the conductometric readings. Such correlation coefficients are known as zero order correlation coefficients, since no attempt is made to eliminate the effect of other variables from any of the reported correlation coefficients.

TABLE I. ZERO ORDER CORRELATION COEFFICIENTS BETWEEN CHEMICAL ASH AND EACH SPECIFIED CONDUCTOMETRIC READING

	ASH	K	K_2	K_3	K_1
Ash		0.9861	0.5974	-0.3318	-0.5486
K			0.6493	-0.2342	-0.4574
K_2				-0.0431	-0.1090
K_3					0.9092

On the assumption that the conductometric readings and the determination of chemical ash are perfectly reliable, it is possible to set up a formula for the solution of the multiple regression equation predicting chemical ash from the conductometric readings, which is the problem of this paper. The data needed for setting up the normal equations to yield the beta weights are the correlation coefficients and the sigmas of each variable. After the weights have been determined, it is a simple matter to determine the constant term. For this, in addition, we need the arithmetic mean of each variable. Table II gives the necessary sigmas and means for the complete solution of the problem.

TABLE II. MEANS AND SIGMAS OF CHEMICAL ASH AND CONDUCTOMETRIC READINGS^a

	MEAN	STANDARD DEVIATION
Ash	9.2658	2.0327
K	592.5953	125.5153
K_2	1447.6308	120.0157
K_3	1561.1677	131.5440
K_1	1594.7046	180.9855

^a These values represent figures obtained from original data. When equation derived from them was used for calculation of ash content, 17 cases fell outside of arbitrarily adopted limits of variability of $\pm 0.30\%$. These samples were redetermined, and in every case errors in manipulation were causes of discrepancies between chemical ash and calculated ash. Final corrected values were used in compiling Table III which shows percentage of cases where conductometric ash checked with chemical ash within certain limits of error. It would be possible to repeat statistical analysis using corrected values, and thus obtain a still better equation. As it is, first approximation is very good, and it seems unnecessary to repeat laborious statistical calculations for slightly higher precision which might thus be obtained.

The formulas necessary for the calculation of the requisite beta weights are given below where the sigmas have the same meaning as before, where r 's represent the correlation coefficient between the variables indicated by the subscripts, and where B_{12} , B_{13} , B_{14} , and B_{15} are the beta weights to be determined.

$$\begin{aligned} r_{\text{ash}(K)} &= 1.000 \frac{\sigma_K}{\sigma_{\text{ash}}} B_{12} + r_{(K)(K_2)} \frac{\sigma_{K_2}}{\sigma_{\text{ash}}} B_{13} + \\ &\quad r_{(K)(K_3)} \frac{\sigma_{K_3}}{\sigma_{\text{ash}}} B_{14} + r_{(K)(K_1)} \frac{\sigma_{K_1}}{\sigma_{\text{ash}}} B_{15} \\ r_{\text{ash}(K_2)} &= r_{(K_2)(K)} \frac{\sigma_K}{\sigma_{\text{ash}}} B_{12} + 1.000 \frac{\sigma_{K_2}}{\sigma_{\text{ash}}} B_{13} + \\ &\quad r_{(K_2)(K_3)} \frac{\sigma_{K_3}}{\sigma_{\text{ash}}} B_{14} + r_{(K_2)(K_1)} \frac{\sigma_{K_1}}{\sigma_{\text{ash}}} B_{15} \end{aligned}$$

$$r_{\text{ash}}(K_3) = r_{(K_3)}(K) \frac{\sigma_K}{\sigma_{\text{ash}}} B_{12} + r_{(K_3)}(K_2) \frac{\sigma_{K_2}}{\sigma_{\text{ash}}} B_{13} +$$

$$1.000 \frac{\sigma_{K_3}}{\sigma_{\text{ash}}} B_{14} + r_{(K_3)}(K_1) \frac{\sigma_{K_1}}{\sigma_{\text{ash}}} B_{15}$$

$$r_{\text{ash}}(K_1) = r_{(K_1)}(K) \frac{\sigma_K}{\sigma_{\text{ash}}} B_{12} + r_{(K_1)}(K_2) \frac{\sigma_{K_2}}{\sigma_{\text{ash}}} B_{13} +$$

$$r_{(K_1)}(K_3) \frac{\sigma_{K_3}}{\sigma_{\text{ash}}} B_{14} + 1.000 \frac{\sigma_{K_1}}{\sigma_{\text{ash}}} B_{15}$$

If we had used as a measure of each variable its deviation from its own mean, we should be able to write the formula directly in deviation form, which would give the deviation of the criterion (chemically determined ash) from its own mean. This, however, was not done. Hence it is necessary to calculate the correction which will give the actual rather than the deviational ash. This is given by substituting in the following equation:

$$C = \text{mean ash} - (B_{12} \text{mean}_K + B_{13} \text{mean}_{K_2} + B_{14} \text{mean}_{K_3} + B_{15} \text{mean}_{K_1})$$

where C is the correctional term to be applied. The required formula then is

$$\tilde{\text{Ash}} = B_{12}S_K + B_{13}S_{K_2} + B_{14}S_{K_3} + B_{15}S_{K_1} + C$$

where $\tilde{\text{Ash}}$ refers to the value of ash to be predicted from the knowledge of the conductometric readings for any given sample. S_K, S_{K_1} , etc., refer to the conductometric readings for a given sample. The degree to which faith can be placed in this formula is indicated by its standard error of estimate, which is a measure of the probable deviation of the predicted value of chemically determined ash from actual determinations of it in all the samples considered. The standard error of estimate is

$$\sigma_{\text{ash}} \sqrt{1 - R_{0.1234}^2}$$

where 0 refers to the chemically determined ash and 1234 refer respectively to K, K_2, K_3, K_1 , and where

$$R_{0.1234} = \frac{B_{12}\sigma_1r_{01} + B_{13}\sigma_2r_{02} + B_{14}\sigma_3r_{03} + B_{15}\sigma_4r_{04}}{\sigma_0}$$

where 0, 1, 2, 3, and 4 have the same meaning as above.¹

Sixty-eight per cent of all cases will lie between plus or minus the standard error of estimate. Ninety-nine per cent of the cases will lie between three times plus or minus the standard error of estimate. (The standard error of estimate for this problem is 0.08).

TABLE III. COMPARISON BETWEEN CHEMICAL ASH AND ASH CALCULATED FROM CONDUCTOMETRIC DETERMINATIONS

CHECKING WITHIN %	PER CENT OF CASES
0.05	20.1
0.10	40.9
0.15	59.7
0.20	77.9
0.25	89.9
0.30	100.0

The relationship as explained above is true only if the variables are perfectly reliably determined. It is improbable that the average between two chemical determinations of ash, which are used as the criterion in this problem, is as reliable as the composite of four conductometric readings.

Table III gives the percentage of cases in which the conductometric ash checked with the chemical ash within specified limits. In order to save space, the complete experi-

¹ $R_{0.1234}$ is known as the multiple correlation coefficient and represents the correlation between the variable to the left of the decimal point in the subscript—i. e., ash—and the best weighted composite of the variables to the right of the decimal point in the subscripts which are the conductometric determinations. It also is the correlation between actual ash values and predicted ash values.

mental data are not presented, but the writers will be glad to furnish them to any one interested.

The agreement between the chemical and the conductometric ash is not quite so good as may be expected from statistical theory, because, as stated above, the prediction holds only if the variables are perfectly reliably determined, which is not the case in experimental work of this character.

It is obvious that knowing the correlation coefficients, one can obtain any regression equation predicting the criterion from the knowledge of any one or any two or three of the conductometric readings taken together. Sample formulas in the deviation form are

$$\begin{aligned} \% \text{ ash} &= 0.9799K - 0.01115K_1 \\ \% \text{ ash} &= 0.96212K - 0.10674K_3 \\ \% \text{ ash} &= 1.0482K - 0.0752K_2 \end{aligned}$$

The multiple correlation coefficients of these equations are, respectively, 0.9922, 0.9921, 0.9943, whereas the multiple correlation for the equation which we have decided to use is 0.99931.

The formula using the variables K, K_2 , and K_3 is as follows:

$$\text{Ash} = 0.016028K - 0.000693K_2 - 0.001518K_3 + 3.14$$

This formula is less reliable than the one we have used. It will yield the value of the ash in 68 per cent of the cases with an error of ± 0.256 . All the cases will be included between the limits of ± 0.768 .

The discrepancy between the previous formula, requiring only three conductance determinations to yield reliable results, and the new one based on four, is attributable to the addition of sucrose in the former case. This addition affects the correlations among the various conductance readings through a change in the variability and mean of each conductance criterion in the presence of the alkali or either of the acids used.

The correlation coefficients among the ash and conductivity values are given in Table IV, which may be compared, relation for relation, with Table I.

TABLE IV. ZERO ORDER CORRELATION COEFFICIENTS BETWEEN CHEMICAL ASH AND EACH SPECIFIED CONDUCTANCE CRITERION IN PRESENCE OF ADDED SUCROSE

ASH	K	K_2	K_3	K_1
K	0.9886	-0.5929	0.9177	-0.3419
K_2		-0.4338	0.9457	-0.2259
K_3			-0.3853	0.9469
K_1				-0.1803

The K_2 values were positively related with ash and K in the series without added sucrose, but are negatively related when sucrose is added. Other changes in relationship occur, indicating that the addition of large amounts of sucrose affects the various conductometric criteria quite differently.

The means and standard deviations of the series with added sucrose are given in Table V, which may be compared with the corresponding Table II, showing the data for the series without added sucrose.

TABLE V. MEANS AND SIGMAS OF CHEMICAL ASH AND CONDUCTOMETRIC READINGS

	(Series with added sucrose)	
	MEAN	STANDARD DEVIATION
Ash	9.1443	1.9863
K	529.7843	111.6370
K_2	1475.1193	165.5589
K_3	1098.7388	98.3436
K_1	1418.0075	115.9811

It is apparent from a comparison of the two tables that the principal difference is in the effect of sucrose on the K_3 reading and to a lesser degree on the K_1 reading. In these two readings, the means and variabilities are significantly reduced.

The maximum deviations of the calculated ash values from those obtained by incineration are ± 0.30 per cent (see Table

III). The highest ash content among all the samples was 14.34 per cent, and the lowest 4.84 per cent. The average for the entire series was 9.27 per cent. The maximum error for an average low-purity product amounts thus to 3 parts in 93, which is much better than the permissible error in the chemical method.

It is undoubtedly possible to attain higher precision in the conductometric ash determinations than in those which form the basis of the comparison—namely, the less accurate and more difficultly reproducible values obtained by incineration. The real meaning of this apparent paradox is that the reproducibility and reliability of the conductance measurements introduce greater consistency among themselves than is to be found among the chemical ash determinations. A striking example is the following application of the above idea: Suppose a sugar of 0.01 per cent ash content were treated with a purified carbon to see whether or not the ash would be reduced by this treatment, and that the carbon actually removed 10 per cent of the total ash. It is at once apparent that in such a case the incineration method would have to furnish data much beyond its order of accuracy, or else excessive quantities of sugar would have to be ashed. On the other hand, a pre-

vious knowledge of the changes in the various conductance values as they are related to changes in ash content would at once furnish an insight into the changes produced by the carbon treatment, even though these changes are exceedingly slight. Moreover, only a small quantity of sample would be required.

ACKNOWLEDGMENT

The writers wish to thank John E. Mull of this laboratory for his kind assistance in making the conductance determinations in the presence of phosphoric acid.

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Graphical Method for Converting Atomic Per Cent into Weight Per Cent

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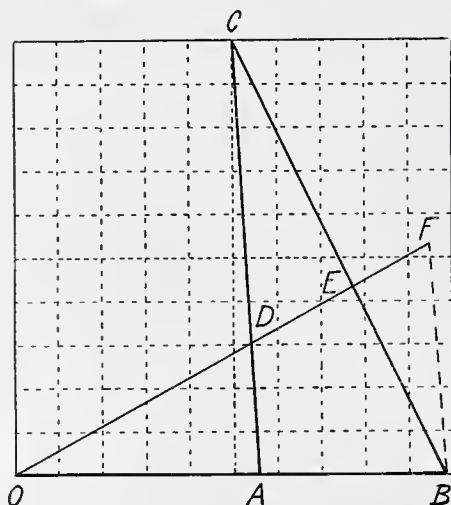
THE following method for converting atomic per cent into weight per cent, and vice versa, seems not to be generally known, and as the numerical calculation is relatively tedious, it seems to be worth communicating.

The theorem of Menelaos states: If OF intercepts the sides of a triangle ABC , the product of the three quotients of the intercepts of each side is

$$\frac{OA}{OB} \cdot \frac{BE}{CE} \cdot \frac{CD}{DA} = 1$$

This is easily proved by making $BF \parallel AC$, when two pairs of similar triangles give

$$BF = \frac{DA \cdot OB}{OA} = \frac{CD \cdot BE}{CE}$$



If we have two substances with the atomic (molecular) weights A and B , mixed in the proportions of atomic per cent a and b ($a + b = 100$), which is weight per cent p and q ($p + q = 100$).

$$\frac{Aa}{Aa + Bb} = \frac{p}{100}$$

This formula will be used for the numerical calculation. It can be transformed into

$$\frac{Aa}{Bb} = \frac{p}{q}, \text{ or}$$

$$\frac{A}{B} \cdot \frac{a}{b} \cdot \frac{q}{p} = 1$$

Now, it is clearly seen how Menelaos' theorem is to be used. On a coördinate paper the atomic weights of the two components are set off on the line OAB . The point C is chosen arbitrarily, but 100 or 200 mm. from OB . If the triangle ABC is completed, the two new sides are divided in per cent by the coördinate net.

Let AD signify p ; i. e., weight per cent of the component A . Then the extension of OD to E gives $BE = a$; i. e., atomic per cent of A . CD and CE are the corresponding quantities for the component B .

But the formula can also be written

$$\frac{A}{B} \cdot \frac{q}{p} \cdot \frac{a}{b} = 1$$

and then BE may signify q and AD , b . The corresponding quantities p and a for A are in this case CE and CD .

One has only to remember that the intercept nearest to the plotted atomic weight is weight per cent of this component, and that the projection on the other side of the triangle is the corresponding atomic per cent.

The line OE will of course not be drawn, but a rule or the edge of a paper will be put through O and the known percentage.

RECEIVED May 4, 1932.

Measuring Microscope for Rubber Specimens

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A MICROSCOPE of low power, equipped with a micrometer eyepiece, affords a convenient and practical means for accurately measuring the dimensions of rubber test specimens, and at the same time permits the inspection of specimens for defects. The equipment here described was designed particularly for measuring the width of the familiar dumb-bell shaped tensile test strips. At the present time no convenient and accurate gage is available for this purpose, and it is common practice to assume that the width of the specimen is the same as the die with which it was cut. The same equipment has been found satisfactory for determining the thickness of test strips, and is generally applicable for the measurement of dimensions up to about 6.4 mm. (0.25 inch).

A microscope provided with a six-times micrometer eyepiece and objectives of 32 and 48 mm. focal length is suitable for measuring the cross-sectional dimensions of rubber test specimens. The width of specimens is usually greater than that of the die with which they were cut. The thickness of soft compounds as determined by the microscope is greater than that indicated by a gage of the plunger type.

appears to be superimposed on it and dimensions may be read directly from the scale. A conversion factor is, of course, employed to convert the observed number of scale divisions to the desired units. The micrometer eyepiece is more convenient than a filar micrometer for work where a very high order of accuracy is not necessary, since the use of the latter

requires the setting of cross-hairs on one edge of the specimen, and the moving of them to the other edge.

SPECIMEN HOLDERS

Suitable specimen holders greatly facilitate the manipulation of samples on the mechanical stage, and insure the samples lying flat without distortion. Two holders for dumb-bell shaped test strips are shown in Figures 1 and 2. One consists of two microscope slides held by spring bronze clips which are attached to the glass by de Khotinsky cement. The clips are so adjusted that an ordinary rubber test strip is held snugly between the slides. The other holder consists of two thick glass slides near whose ends grooves are cut so that the slides with a specimen between them may be held together with rubber bands. The rubber bands do not project above the surface of the glass, since they would interfere with the free movement of the holder by the mechanical stage. Both specimen holders are so designed that measurements may be made on either side of a sample without removing it from

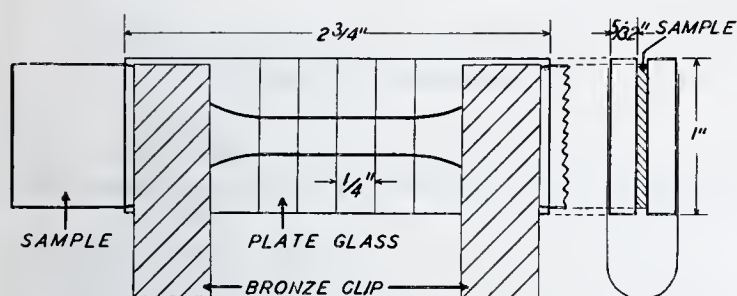


FIGURE 1. SPECIMEN HOLDER OF GLASS PLATES HELD TOGETHER WITH BRONZE CLIPS

This use of the microscope embodies no original features. The method and equipment, however, are here described in some detail, since they may be of interest to investigators who may have occasion to make accurate mechanical measurements on rubber.

It is not the purpose of the present discussion to make a critical comparison of dimension-measuring devices employed in connection with test specimens of rubber. Some comparative measurements are cited which indicate that the microscope affords an improvement in accuracy over existing methods, but consideration is not given here to the general subject of the probable errors in rubber testing.

THE MICROSCOPE

The microscope is of low power in order that a relatively wide field of view may be obtained. It consists of a standard microscope body fitted with a six-times micrometer eyepiece and objectives of 48 and 32 mm. focal length. With the former objective and a tube length of 160 mm., the field of view is 9.3 mm. in diameter, and the magnification 13 diameters; with the latter objective, the field is 5.4 mm. in diameter and the magnification 24 diameters. The equipment includes a mirror and a mechanical stage.

The micrometer eyepiece is a standard eyepiece on the diaphragm of which is cemented a glass disk ruled with a scale 10 mm. in length which is ruled in 100 subdivisions. The eyepiece is provided with a focusing eye-lens in order to accommodate the micrometer scale to the eye of the observer. When an object is viewed under the microscope, the scale ap-

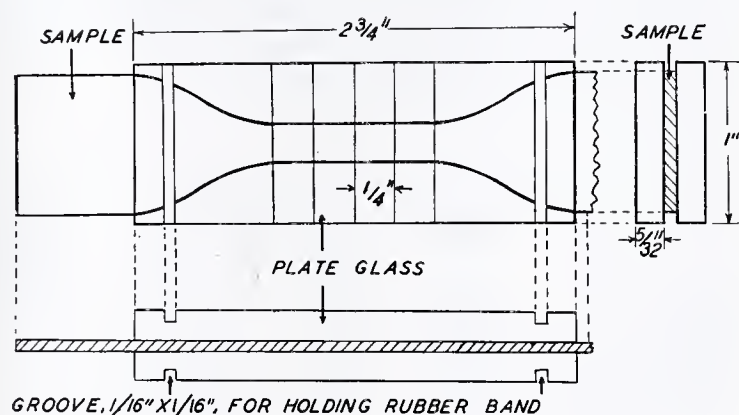


FIGURE 2. SPECIMEN HOLDER OF GLASS PLATES HELD TOGETHER WITH RUBBER BANDS

the holder. The slides are ruled so that measurements may be made at definite intervals along the length of specimens under observation.

METHOD OF MAKING MEASUREMENTS

The scale of the micrometer eyepiece is conveniently calibrated by comparison with a stage micrometer which is ruled on a glass slide. The calibration factor is dependent on the length of the draw tube of the microscope, and consequently may be adjusted to a convenient number by the proper setting of the draw tube. In the case of the equipment described herein, the calibration factor for the 32-mm. objective ranges from 0.0373 mm. per scale division for a 150-mm. tube length, to 0.0470 mm. for a tube length of 170 mm., and has the con-

venient value, 0.0400 mm. per scale division, when the tube length is adjusted to 161.7 mm.

In making measurements, the specimen under examination is mounted in a holder and located in the middle of the microscope field with the proper focus, at which the scale and the surface of the specimen appear in the same plane and show no relative displacement as the eye is moved from one side of the eyepiece to the other. The eyepiece is then rotated so as to bring the scale across the specimen in the direction in which measurement is desired. If the edges of the specimen are clean-cut, readings may be estimated to 0.1 scale division, although a reading to 0.5 scale division, which may be made almost at a glance, is equivalent to a precision of 0.5 per cent if the object covers the full scale. If the sample has been placed symmetrically in the holder, a length of several centimeters may be brought into the field by lateral motion of the mechanical stage. This permits the cut edges to be scrutinized for irregularities, and facilitates the making of measurements at a number of points along a strip.

The microscope may be readily employed for examining and measuring the dimensions of a die. It is only necessary to remove the stage and mirror and mount the die in the field of vision. The difficulty of focusing sharply on the edges of the die may be obviated by placing a glass slide across the die and bringing the lower surface of the glass into focus by observing marks on it.

ILLUSTRATIVE MEASUREMENTS

Measurements of the width of the constricted portion of several dumb-bell shaped dies and of specimens cut with them were made by means of the microscope. The specimens were prepared from three rubber compounds having different degrees of hardness: a pure gum compound, a compound containing 24 per cent of titanox pigment by volume, and one containing 20 per cent of micronex by volume. The hardness values, as determined by the Shore instrument, were 48, 60, and 75, respectively. The dies employed were taken at random from those in routine use, and the samples were cut with an arbor press. The widths which are given in Table I are each the average of three measurements made near the center of the constricted portion of the dies or the specimens.

TABLE I. WIDTH OF RUBBER TEST SPECIMENS AND DIES

OBJECTS MEASURED	POSITION	WIDTH			
		Die 1	Die 2	Die 3	Die 4
		<i>Mm.</i>	<i>Mm.</i>	<i>Mm.</i>	<i>Mm.</i>
Dies		6.58	6.43	6.54	6.45
Micronex rubber samples	Top	6.68	6.44	6.48	6.48
	Bottom	6.68	6.48	6.48	6.38
Titanox rubber samples	Top	6.64	6.46	6.48	6.48
	Bottom	6.84	6.74	6.72	6.55
Pure gum rubber samples	Top	6.64	6.46	6.49	6.50
	Bottom	6.82	6.68	6.69	6.58

The results indicate that the specimens are on the average wider than the die with which they were cut, the upper side being about the same width as the die, but the lower side being appreciably wider in the case of the softer compounds. The mean of the top and bottom widths was in several instances as much as 0.10 to 0.15 mm. greater than the width of the die, hence the possible error which might arise from this source would be of the order of 2 per cent if the width of the test specimen were assumed to be the width of the die. This estimate leaves out of consideration the fact that the edges of specimens cut with a die are usually somewhat concave. At the time of measurement, however, it is possible to make qualitative observation of the degree of concavity.

Measurements of thickness were made with the microscope on some of these same specimens, mounted on edge in a slot in a wooden block. A comparison of the values found with

the thickness as indicated by a dial gage of the plunger type is given in Table II. This gage was provided with a contact foot 6.4 mm. (0.25 inch) in diameter, and was actuated by a load of 85 grams (3 oz.). In the case of the soft, pure gum stock, the thickness indicated by the microscope was of the order of 2 per cent greater than the thickness indicated by the gage, as would be expected from the evident compression by the contact foot. In the case of the stiffer stocks, the measurements by the microscope and the gage were in reasonably close agreement. In some instances the thickness indicated by the gage was somewhat the greater. This may have been owing in part to bloom and dust particles on the surface of the specimens.

TABLE II. COMPARATIVE MEASUREMENTS OF THICKNESS

SPECIMEN	THICKNESS	
	By microscope <i>Mm.</i>	By plunger type gage <i>Mm.</i>
Pure gum	1	2.13
	2	2.06
	3	2.08
	4	2.07
Titanox	1	1.40
	2	1.34
	3	1.41
	4	1.32

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Modification of Poth's Carbon Dioxide Generator

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IN A recent paper, Poth (1) described an apparatus for the generation of very pure carbon dioxide. Operation of several of these generators in this laboratory has brought to light several undesirable features: (1) The pressure at which the carbon dioxide is delivered varies considerably, owing to the rise and fall of the acid in tube *C* of Figure 1; (2) the apparatus is rather fragile, exhibiting a tendency to break at point *D* because of strains in the glass, and at *B* and *C* because of jars and strains which occur in handling; (3) a cup-like mass of crystals forms at point *A* during continuous operation of the generator, causing accumulation of acid and resulting in erratic operation; (4) the lack of a reservoir at *E* allows mercury to be drawn from trap *F* into the sulfuric acid bulb in case of a large drop in temperature.

To eliminate these defects in an otherwise excellent piece of apparatus, a number of modified generators have been constructed and tried out.

The one which has proved most satisfactory is shown in Figure 2. The two large bulbs are made from 1- and 2-liter flasks. Spout *L* is best made from tubing of 2 mm. inside diameter, and should not be more than 1 cm. from bend to tip. Tube *N* should have an inside diameter of 5 or 6 mm. Bulb *O* should have an outside diameter of about 30 mm., and trap *R* should have a depth of 14 or 15 cm. and a capacity of at least 20 cc.

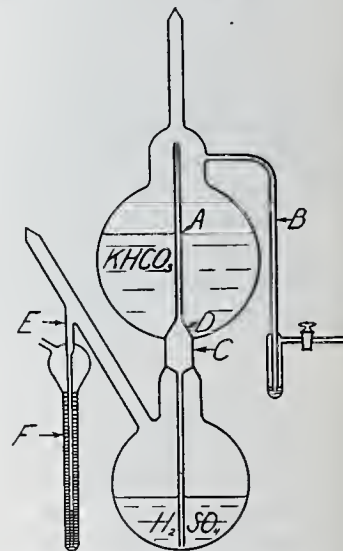


FIGURE 1. POTH GENERATOR

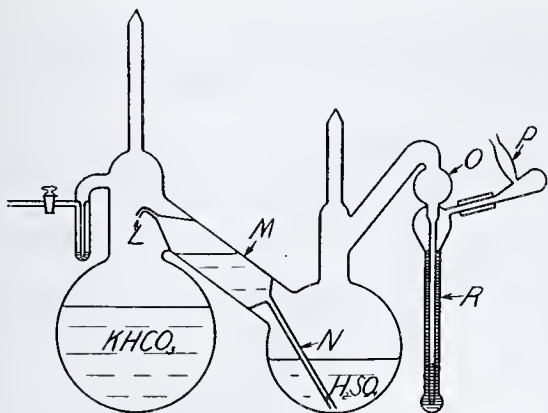


FIGURE 2. MODIFIED GENERATOR

of mercury. The apparatus, if reasonably well built, will stand fairly rough treatment. It needs no mounting other than two

cork rings as support for the two large bulbs, and is easily carried about, using neck *M* as a handle. A safety trap, *P*, is provided to prevent loss of mercury in case a considerable amount of carbon dioxide blows through the pressure regulator, *R*.

This generator is charged and operated in exactly the same manner as the Poth apparatus, except that, owing to the relatively large volume of chamber *M*, 200 cc. of water and 200 cc. of concentrated sulfuric acid are placed in the smaller bulb, instead of 170 cc. of each, as recommended by Poth.

LITERATURE CITED

- (1) Poth, *IND. ENG. CHEM., Anal. Ed.*, 3, 202 (1931).

RECEIVED January 14, 1932. Mr. Lowe is a Julius Stieglitz Fellow at the University of Chicago. Financial assistance in this work was received from the Julius Stieglitz Fund for Research in Chemistry Applied to Medicine, established at the University of Chicago by the Chemical Foundation.

Detection and Determination of Free Sulfur in Petroleum Distillates

A Colorimetric Method

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VARIOUS substances in gasoline and other petroleum products which cause corrosion of metals have been investigated (1). Many of these substances may be determined directly, whereas others have to be estimated by indirect methods. Among the substances that cause corrosion are hydrogen sulfide and free sulfur. The former may be determined directly and rapidly by well-known analytical methods, but for the determination of the latter, the direct methods are long and tedious and are seldom used. The copper strip test, an indirect method, is used more frequently.

In searching for a reaction which could be used as the basis of a direct qualitative and quantitative method for the determination of sulfur and which would be both rapid and accurate, the Halphen method for the detection of cottonseed oil was studied. Sulfur is one of the reagents in this test. Since this seemed to offer the necessary basis, an obvious modification of this reaction was tried for the detection and determination of free sulfur in naphthas.

PROCEDURE

REAGENT. Mix 80 cc. of refined unbleached cottonseed oil, 80 cc. of freshly distilled carbon disulfide, and 8 cc. of pyridine, and place in a glass-stoppered bottle. This mixture should be made fresh every day and kept cool in the dark when not in use, as it decomposes upon standing.

STANDARD SOLUTIONS. Prepare odorless, purified naphtha by distilling over metallic sodium. Dissolve one gram of sulfur in 1000 grams of naphtha and prepare solutions of sulfur containing 0.010, 0.025, 0.050, 0.075, and 0.100 gram of sulfur in 100 grams by suitable dilutions with sulfur-free naphtha. It must be cautioned that standard solutions of sulfur in purified naphtha are not stable and that in some cases, at least, corrosive naphtha becomes noncorrosive on aging.

PROCEDURE. Place 20 cc. of the oil to be tested in an oil-sample bottle, add 4 cc. of the sulfur reagent, and heat for 30 minutes at 100° C. The standard solutions with which the oil is to be compared should be treated similarly and run simul-

taneously. At the same time, heat 20 cc. of the oil to be tested and one of the standards to which no reagent has been added to insert in the comparator to correct for any color that may be developed from the heat on the oils. After heating for 30 minutes, add sufficient water-white gasoline to the sample to bring the volume to 25 cc., and compare with the color developed by the standards which have been treated similarly.

QUANTITATIVE TESTS

In making quantitative tests, weighed amounts of sulfur varying from 0.025 to 0.100 per cent were added to sulfur-free naphtha and the mixture shaken until the sulfur was dissolved. Then 20 cc. of each sample were treated with 4 cc. of stock reagent, and the mixture heated at 100° C. for 30 minutes. The volumes were then made up to 25 cc. and the colors compared. The depth of color increased with the content of sulfur. The total sulfur was also determined by the lamp method, in which 5 to 12 grams of sample were taken, depending upon the amount of sulfur present. The sulfur found in the original naphtha by the lamp method was subtracted from the total sulfur in the solution to obtain the free sulfur. The results are shown in Table I.

TABLE I. RELATION BETWEEN FREE SULFUR IN NAPHTHA AS FOUND BY COMBUSTION AND BY COLORIMETRIC METHOD

	S ADDED TO 100 GRAMS OF NAPHTHA	S BY COLOR	TOTAL S BY LAMP	FREE S BY LAMP	DIFF. BETWEEN S BY COLOR AND LAMP
	Gram	%	%	%	%
1	None	None	0.003	None	
2	0.010	0.0095	0.012	0.009	+0.0005
3	0.025	0.026	0.027	0.024	+0.002
4	0.050	0.050	0.052	0.0495	+0.0005
5	0.075	0.0745	0.078	0.075	-0.0005
6	0.100	0.103	0.104	0.101	+0.002

These tests showed that the results by the colorimetric method agree with both the quantity of sulfur added and the free sulfur found by the lamp method.

Tests were made to ascertain whether other sulfur com-

pounds would interfere with the reaction. The compounds of sulfur used were hydrogen sulfide, mercaptans, sulfuric esters, organic sulfides, disulfides, sulfonic acids, and sulfones in concentrations varying from 0.1 to 3.0 per cent in the naphtha. They were treated with the reagent by the process described above, but in no case did pink or red color develop. The modified Halphen method can therefore also be used for the qualitative detection of free sulfur in light petroleum distillates.

DISCUSSION

In making these tests, it was found that excessive dilution of the standards after the color had developed gave low results. In no case should the standard be diluted with water-white naphtha to more than one and one-half times its original volume in making the comparisons.

If the percentage of free sulfur is over 0.15 per cent, a brownish precipitate forms which does not redissolve readily. Hence, if the free sulfur is high, the sample should be diluted prior to analysis.

In making the colorimetric comparisons, a heated tube of the untreated naphtha should be placed in front of the standard and a heated tube of the untreated standard should be placed in front of the sample to compensate for any darkening of the oils by heating.

Samples of stock reagent stored in an ice box have not shown any evidence of deterioration after 48 hours, but it should be made fresh every day.

LITERATURE CITED

(1) Garner, F. H., *J. Inst. Petroleum Tech.*, 17, 451-63 (1931).

RECEIVED July 25, 1931.

Remmey Oxy-Acetylene Test Furnace for Coal Ash Fusion Point Determination

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THE introduction of the Remmey furnace (4) to the ceramic industry and its subsequent success in this field has led to the investigation of its possible use for coal ash fusion determinations. Acetylene and oxygen are the fuels used with this furnace. The entire weight of the apparatus exclusive of oxygen and acetylene tanks is about 150 pounds (68 kg.), and it can be moved from one place to another without damage to the furnace or any of its connections. It is sturdily constructed and built to withstand temperatures as high as 3320° F. (1827° C.) (Cone 37). The floor space needed is approximately 3 1/3 square feet (0.3 sq. meter) and must be near a supply of water for the circulating cooling system.

The furnace is placed on a metal table with an asbestos top. Regulators on the oxygen and acetylene tanks are set to deliver the gases at 16 and 10 lb. per sq. in. (1.12 and 0.7 kg. per sq. cm.) pressure, respectively, to the connecting hose which leads to the synchronized valves of the furnace. These valves are attached to the front of the table and are so connected that when one valve is opened or closed the other valve is opened or closed a corresponding amount. From the synchronized valves the gases enter a mixer attached to the under side of the table and then pass into the firebox through the water-cooled tips of the burner. Between the synchronized valves is a secondary oxygen valve which is used only in starting. An excess of oxygen is needed only at the start of a run or in

special cases where a highly oxidizing atmosphere is desired at all times.

The mixed gases enter the furnace at a tangent to the inner wall and consequently take a rotary motion around the center post on which the plaque and test cones are placed.

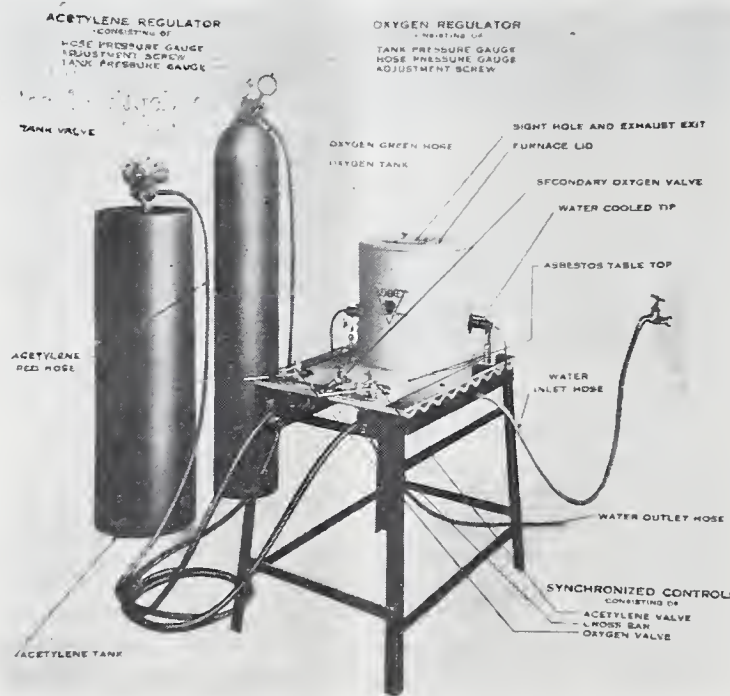
There is but one opening in this furnace when assembled. A hole 0.75 inch (2 cm.) in diameter, directly over the plaque, serves as a sight hole as well as an outlet for exhaust gases. With the aid of dark glass such as is used by acetylene welders, the operator is able to observe the test cones with no difficulty. The heat from the furnace is not noticeable and makes possible the use of this apparatus in any chemical laboratory without discomfort to other employees.

PROCEDURE

In this investigation two series of tests were carried out. Series A, consisting of thirteen samples, was carried out in June, 1932, with J. L. Porter as operator. Series B, consisting of twelve samples, was carried out in August, 1931, with F. M. Taylor as operator.

In carrying out Series A, none of the melting points or softening temperatures were known until after the results were reported to the Bureau of Mines. In Series B, the fusion temperatures were known to the operator at the time the tests were made.

The ash cones were prepared as directed in Technical Paper 8 of the Bureau of Mines (6). Ready-made plaques were



REMMEY OXY-ACETYLENE TEST FURNACE

TABLE I. RESULTS WITH SERIES A

BUR. MINES IDENTIFICATION NO.		GAS FURNACE METHOD				REMMEY FURNACE METHOD				
		Fusion temp. (Bur. Mines)		Difference		Fusion temp.		Cone No.	Difference	
		° F.	° C.	° F.	° C.	° F.	° C.		° F.	° C.
1	A-78161	1996 2008	1091 1098	12	7	1975 1975	1079 1079	0.03 0.03	0	0
2	A-78101	2124 2152	1162 1178	28	16	2065 2080	1129 1138	1-2 2+	15	9
3	A-78442	2199 2219	1204 1215	20	11	2150 2160	1180 1182	5 5+	4	2
4	A-78099	2277 2284	1247 1251	7	4	2218 2225	1214 1218	7+ 7-8	7	4
5	A-78369	2367 2347 2372	1297 1286 1300	Max. 25 Min. 5	14 3	2282 2291	1250 1255	9 9-10	9	5
6	A-78257	2448 2458 2444	1342 1348 1340	Max. 14 Min. 4	8 2	2300 2295	1260 1257	10 10 -	5	3
7	A-78256	2552 2541 2523	1400 1394 1384	Max. 29 Min. 11	16 6	2462 2450	1350 1343	13 13 -	12	7
8	A-78151	2611 2610 2615	1433 1432 1435	Max. 5 Min. 1	3 1	2426 2450	1330 1343	12-13 13 -	24	13
9	A-78436	2689 2678	1476 1470	11	6	2565 2570	1407 1410	15 - 15	5	3
10	A-75590	2752 2790	1511 1532	38	21	2705 2720	1485 1493	18 18+	15	8
11	A-77864	2806 2793	1541 1534	13	7	2690 2705	1477 1485	18 - 18	15	8
12	A-76869	3015 3000	1657 1649	15	8	2912 2921	1600 1605	26-27 27	9	5
13	A-75479	2962 2993	1628 1645	31	17	2935 2939	1613 1615	28 - 28	4	2
				Av. 17	9	Av. 9.5 5				

purchased from the manufacturers of the Remmey furnace. The plaques are approximately 2¹¹/₁₆ inches (6.84 cm.) in diameter, with a hole three-sixteenths inch (0.5 cm.) in diameter in the center, 0.125 inch (0.02 cm.) thick. There are places for twenty Standard pyrometric cones (small size) about 0.125 inch (0.02 cm.) from the edge of the plaque. The cost of these plaques is about 12 cents each, but the convenience of having the plaque ready for use and the fact that each plaque can be used for more than one ash fusion is a great saving in time. A temperature of over 3000° F. (1649° C.) has no effect on the plaque.

The furnace was started according to directions supplied with each furnace by the manufacturer. The directions for the change in the valves were closely followed until the inside of the furnace came to a red heat. A pyrometer was inserted in the top of the furnace before Series A was run, and the settings recorded, so that a rise of not more than 20° C. per minute could be maintained when within the fusion point range of any cone. For example, it was found

that when the valves were set at 44 on the scale, a rise of 18° C. was maintained, falling in rate of rise slowly until about 1800° F. (983° C.) was reached. Then the setting was advanced by fives gradually until the higher temperatures were reached.

TABLE II. AVERAGES WITH SERIES A

	AV. TEMP. (BUR. MINES)		AV. TEMP. (REMMEY)		DIFFERENCE		ERROR %
	° F.	° C.	° F.	° C.	° F.	° C.	
1	2002	1095	1975	1079	- 27	-16	-1.35
2	2138	1170	2073	1134	- 65	-36	-3.04
3	2209	1210	2158	1181	- 51	-29	-2.30
4	2281	1249	2222	1216	- 59	-33	-2.58
5	2362	1294	2287	1253	- 75	-41	-3.17
6	2450	1343	2298	1259	-152	-84	-6.20
7	2539	1393	2456	1347	- 83	-46	-3.26
8	2612	1434	2438	1336	-174	-98	-6.65
9	2684	1473	2568	1409	-116	-64	-4.32
10	2771	1521	2713	1489	- 58	-32	-2.09
11	2800	1545	2698	1481	-102	-64	-3.62
12	3008	1651	2917	1603	- 91	-48	-3.02
13	2978	1636	2937	1614	- 41	-22	-1.37
				Av. - 84	-47	-3.34	

TABLE III. RESULTS WITH SERIES B

BUR. MINES IDENTIFICATION No.		GAS FURNACE METHOD				REMMEY FURNACE METHOD				
		Fusion temp. (Bur. Mines)		Difference		Fusion temp.		Cone No.	Difference	
		° F.	° C.	° F.	° C.	° F.	° C.		° F.	° C.
1	A-54455	2053 2025	1123 1106	28	17	2057 2025	1125 1107	1 0.01 —	32	18
2	A-54442	2170 2176	1187 1191	6	4	2200 2210	1204 1210	7 — 7	10	6
3	A-70080	2269 2244	1243 1229	25	14	2260 2260	1238 1238	8-9	0	0
4	A-70849	2314 2331	1268 1278	17	10	2350 2337	1288 1281	11-12 11 +	13	7
5	A-54454	2376 2413	1302 1323	37	21	2462 2462	1350 1350	13	0	0
6	A-70837	2491 2484	1366 1362	7	4	2534 2500	1390 1371	14 13-14	34	19
7	A-70035	2520 2498	1382 1370	22	12	2534 2525	1390 1385	14 14 —	9	5
8	A-71082	2547 2550	1397 1399	3	2	2570 2570	1410 1410	15	0	0
9	A-54439	2601 2590	1427 1421	11	6	2642 2650	1450 1454	16 16 +	8	4
10	A-54451	2649 2649	1454 1454	0	0	2680 2685	1471 1474	17 +	5	3
11	A-54449	2674 2671	1468 1466	3	2	2705 2705	1485 1485	18	0	0
12	A-71081	2907 2885	1597 1585	22	12	2900 2900	1593 1593	26 —	0	0
				Av. 15	8					
						Av 9 5				

Just as the test cone had slumped down into a spherical mound the furnace was shut off and a portion of the top plate removed so as to stop the heating of the cones suddenly. The fusion temperature was taken from the cone which had leaned to a position where the tip had touched the plaque.

In Series A, where none of the fusion temperatures were known, one run had to be made to find the approximate fusion temperature. This was done by mounting the test cone on a plaque with at least five different Standard cones. The color of the ash cone gave an indication of whether the ash would have an exceedingly low melting point or not. This aided somewhat in deciding whether to put in the cones at the lower or higher end of the range. After the approximate temperature was found, two check runs were made on each ash cone using the Standard cones which had a fusion point close to the ash cone.

TABLE IV. AVERAGES WITH SERIES B

	AV. TEMP. (BUR. MINES)		AV. TEMP. (REMMY)		DIFFERENCE		ERROR %
	° F.	° C.	° F.	° C.	° F.	° C.	
1	2039	1115	2041	1116	2	1	+0.10
2	2173	1189	2205	1207	32	18	+1.50
3	2256	1236	2260	1238	4	2	+0.18
4	2322	1272	2344	1284	22	12	+0.95
5	2394	1312	2462	1350	68	38	+2.84
6	2488	1367	2517	1381	29	14	+1.16
7	2509	1376	2530	1388	21	12	+0.84
8	2549	1398	2570	1410	21	12	+0.82
9	2596	1424	2646	1452	50	28	+1.93
10	2649	1454	2683	1473	34	19	+1.28
11	2673	1467	2705	1485	32	18	+1.20
12	2896	1591	2900	1593	4	2	+0.14
Av. 26.6					14.7		+1.08

In Series B, the softening temperatures as determined by the Bureau of Mines by the gas furnace method (1) were known, and no preliminary test had to be run. The fusion temperature was then obtained, usually in two successive runs.

DISCUSSION

Since heating up the cone to red heat does not affect the final fusion temperature, this furnace needs to be cooled only to around 1500° F. (816° C.) before the next run is started. The time consumed in cooling the furnace to this temperature is comparatively short. Twelve fusions may be run in a working day of eight hours if this method is followed.

The temperature attained in one determination in this investigation was 2900° F. (1593° C.). To make this run, 60 cubic feet (1.7 cubic meters) of oxygen and 25 cubic feet (0.7 cubic meter) of acetylene were consumed when the furnace was started at room temperature. This represents a cost of \$1.10 for fuel. When the plaque was placed in the furnace at about 1500° F. (816° C.), it required 36 cubic feet (1 cubic meter) of oxygen and 17 cubic feet (0.5 cubic meter) of acetylene to reach the same fusion point. This represents a fuel cost of only 70 cents for the test. When starting from room temperature, the secondary oxygen valve is opened until the furnace reaches dull red heat and much more oxygen is used. When the furnace is already hot, no excess oxygen has to be supplied.

A particular advantage of the oxy-acetylene method is its suitability for places where no manufactured or natural gas is available. Another advantage is evident in the heat insulation. This is better than is usually provided for commercial gas furnaces. No attempt is made to compare the cost of the oxy-acetylene method with the A. S. T. M. method, for no manufactured or natural gas was available.

In the comparison of the gas-furnace and the micropyrometer methods (2) and the comparison of the gas-furnace and De Graaf electric coal ash fusion furnace (5), reducing atmospheres were used and were considered necessary if comparable results were to be obtained. The gases from this

furnace were analyzed several times, but in each case atmospheric oxygen could not be excluded, owing to cracks in the wall next to the gas nozzle.

Table I gives the number of each sample for Series A as recorded at the Bureau of Mines, the fusion temperatures by each method, the differences in temperature for duplicate runs, and the average difference in duplicate runs by each method. Table II gives the two results obtained by each method, the error in the temperature recorded by the Remmey method (assuming the Bureau of Mines temperature average to be correct), the percentage error in each of thirteen samples, and the average percentage error. Tables III and IV give corresponding data for Series B.

CONCLUSIONS

It is regrettable that the operator of Series A did not run several samples with known fusion points before the series was started, or at least before the series was reported. This undoubtedly would have brought both series nearer together, for it is apparent that in the plaques in Series A the ash cones were not carried to the same degree of softness as in Series B.

A sample of coal ash with known fusion point must always be used in establishing the appearance of the ash cone at what is to be called the fusion temperature. The fact that all results in Series A were below, and all those in Series B were above the results obtained in the gas-fired furnace, although checking closely within themselves, emphasizes the need of further work by some one person who has both methods available and who is accustomed to reading the fusion temperatures by both methods. Another series of tests should be run by the same person by both methods so that the condition of the ash cone at fusion temperature as defined in Technical Paper 8 of the Bureau of Mines will be identical in both methods. Since no gas for use as fuel is available at this station, the above suggestion cannot be carried to completion at the Virginia Polytechnic Institute.

Table V gives the numbers and corresponding fusion temperatures of the cones available for such tests.

TABLE V. STANDARD PYROMETRIC CONE EQUIVALENTS

CONE No.	P. C. E. ^a		CONE No.	P. C. E. ^a	
	° F.	° C.		° F.	° C.
0.03	1975	1080	16	2642	1450
0.02	2003	1095	17	2669	1465
0.01	2030	1110	18	2705	1485
1	2057	1125	20	2768	1520
2	2075	1135	23	2876	1580
3	2093	1145	26	2903	1595
4	2129	1165	27	2921	1605
5	2156	1180	28	2939	1615
6	2174	1190	29	2984	1640
7	2210	1210	30	3002	1650
8	2237	1225	31	3056	1680
9	2282	1250	32	3092	1700
10	2300	1260	33	3173	1745
11	2327	1275	34	3200	1760
12	2390	1310	35	3245	1885
13	2462	1350	36	3290	1810
14	2534	1390	37	3320	1825
15	2570	1410			

NOTE: Cones 19, 21, 22, 24, and 25 not made. The average difference between cones in this series of 35 is 33° F. or 18° C.

^a Pyrometric Cone Equivalent (P. C. E.) of cones manufactured by Standard Pyrometric Cone Company, 1445 Summit St., Columbus, Ohio.

ACKNOWLEDGMENT

The authors wish to express their appreciation to A. C. Fieldner and H. M. Cooper of the Bureau of Mines, Pittsburgh, who furnished the ash samples and the fusion temperatures which they obtained by the Bureau of Mines method, to the Ceramic Engineering Department of the Virginia Polytechnic Institute for their assistance and use of their equipment and laboratory in this investigation, and to O. C. Burkhart for his assistance in preparing the cones for Series A.

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Improved Distillation Trap

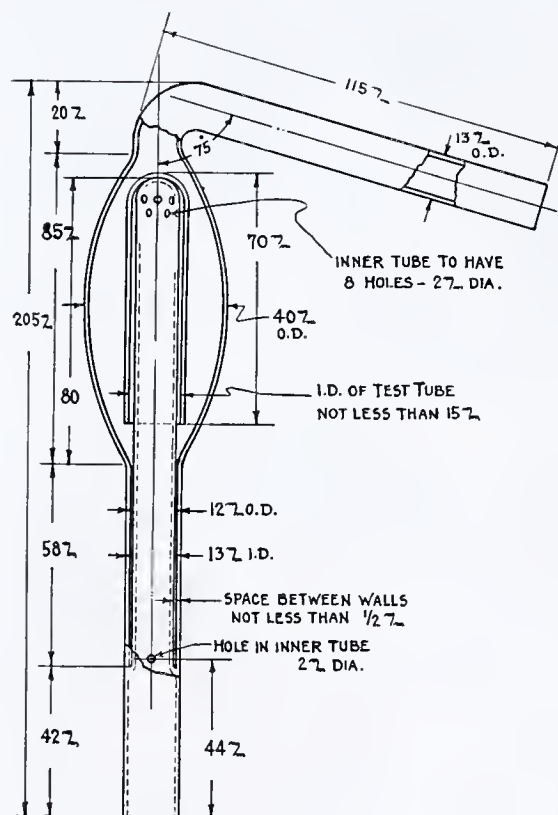
EDWARD S. WEST, Washington University School of Medicine, St. Louis, Mo.

THE diagram represents a trap for use as a connecting bulb in Kjeldahl distillations which has been found superior to the ones in common use. It was originally used in a still for conductivity water and is now employed by the writer wherever an efficient distillation trap is required. It has the advantage of operating entirely without spattering and of efficiently removing fine spray from the vapors. The apparatus is easily made.

In operation, vapors pass up the inner tube, through the side holes at the end, and are deflected down through the wet narrow annular space between the inner tube and cap. The vapors again change direction at an angle of 180 degrees and pass out between the wet walls of the cap and bulb. Condensed liquid returns to the boiling flask through a hole at the bottom of the inner tube near its seal to the outer tube. The space between the walls of the inner and outer tubes, around and above this hole, must be sufficiently narrow to hold by capillarity a column of water which will prevent steam blowing through it.

The dimensions given are satisfactory, but may be varied rather widely except that the space between the inner and outer tubes must not be too wide, nor the return hole too large, and the exit holes at the end of the inner tube must be large enough to allow passage of the vapors at a low pressure to prevent blowing through the return hole. Traps with practically any desired efficiency may be made by simply lengthening the inner tube and cap.

This apparatus may be obtained from Arthur H. Thomas Company, Philadelphia, Pa.



RECEIVED July 26, 1932.

An Identification Test for Oxalic Acid

EARLE R. CALEY, Frick Chemical Laboratory, Princeton University, Princeton, N. J.

SINCE several carboxylic acids form more or less insoluble calcium salts, the usual calcium oxalate precipitation test for oxalic acid is not an especially distinctive means for identifying the acid, and may lead to confusion in certain instances. The following specific precipitation reaction for free oxalic acid is based upon the fact that sodium oxalate is a sparingly soluble salt, whereas the normal sodium salts of practically all other known carboxylic acids are freely soluble in water.

Dissolve 0.10 gram of the solid organic acid in 2.0 cc. of cold water and add 1.0 cc. of approximately 6 *N* sodium hydroxide solution. Shake the mixture vigorously for 1 or 2 minutes. The separation of a white crystalline precipitate indicates oxalic acid.

The proportions of weights and volumes given were those found to give the optimum results in a series of experiments bearing on this point. Any marked deviations from these details may vitiate the test. The weights and volumes may,

of course, be reduced in proper proportion in case a sample as large as 0.10 gram is not available for examination.

This reaction is not of value for the detection of oxalic acid in mixtures, but is intended solely as a simple identification test for the free acid in order to distinguish it readily from other solid, water-soluble, carboxylic acids. Tests made on a number of such acids using this procedure yielded negative results even when samples larger than 0.10 gram were taken. Among those examined were the following representative ones: citric, crotonic, glycollic, maleic, malic, malonic, mandelic, succinic, and tartaric. As far as the writer has been able to determine, the only carboxylic acid that will give a precipitate in the above test is dihydroxytartaric acid. However, it is not likely that confusion could arise from this source in view of the unstable character of this acid and the special means required to obtain it.

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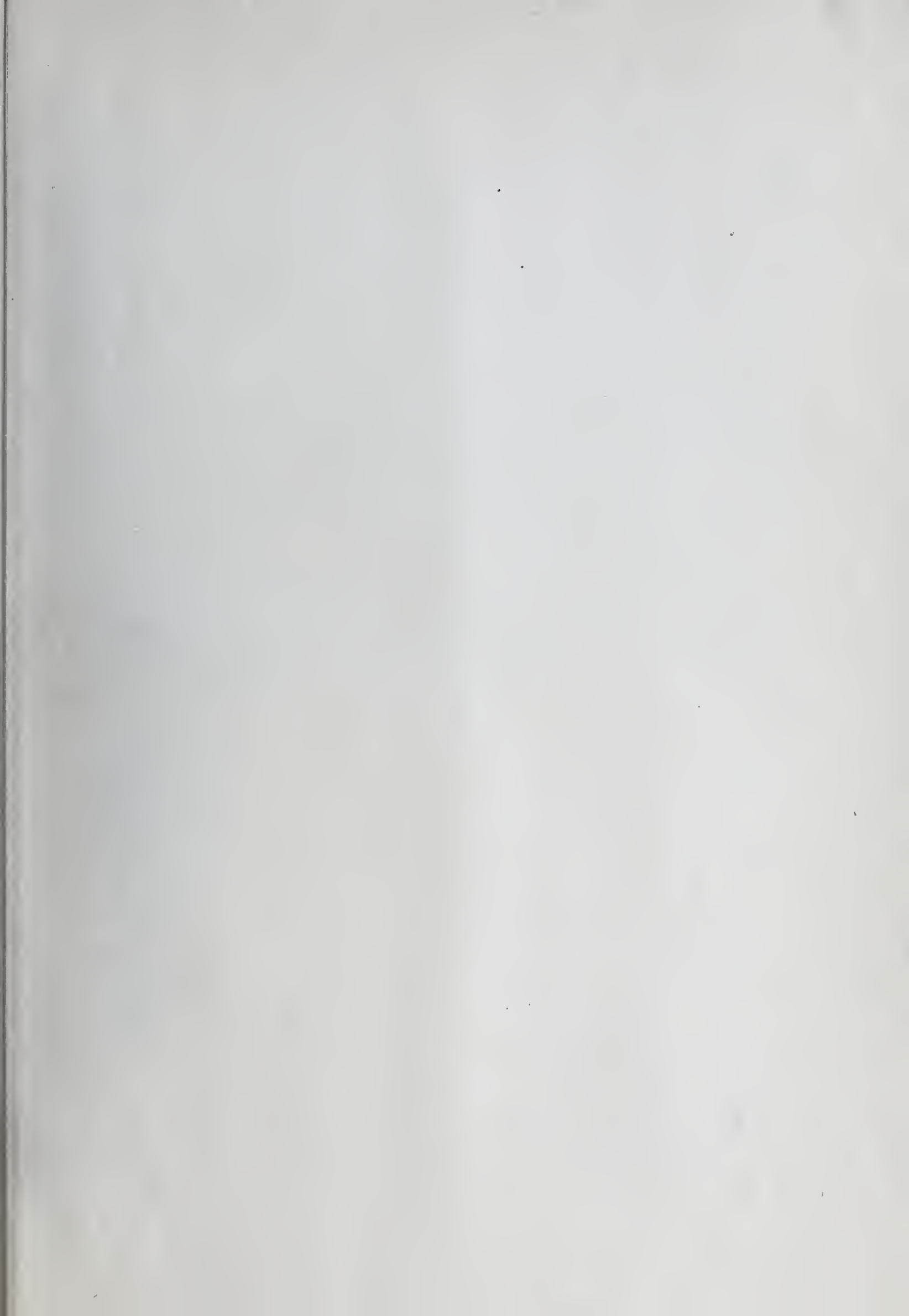
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